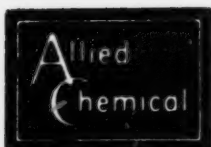


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APPLICABILITY OF REDUCTION TO SULFUR  
TECHNIQUES TO THE DEVELOPMENT OF  
NEW PROCESSES FOR REMOVING SO<sub>2</sub>  
FROM FLUE GASES

Final Report - Volume II  
Phase II of Contract PH-22-68-24



**INDUSTRIAL CHEMICALS DIVISION**

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November 1970

For:

New Process Development Section  
Division of Process Control Engineering  
National Air Pollution Control Administration  
U. S. Department of Health, Education, and Welfare

Industrial Chemicals Division  
Allied Chemical Corporation



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| <b>BIBLIOGRAPHIC DATA SHEET</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 1. Report No.<br><b>APTD-0660</b> | 2.                                                      | 3. Recipient's Accession No.   |
| 4. Title and Subtitle<br><b>Applicability of Reduction to Sulfur Techniques to the Development of New Processes for Removing SO<sub>2</sub> From Flue Gases Volume II</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                   | 5. Report Date<br><b>September 30, 1970</b>             |                                |
| 7. Author(s)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                   | 6.                                                      |                                |
| 9. Performing Organization Name and Address<br><b>Industrial Chemicals Division<br/>Allied Chemical Corporation<br/>P. O. Box 405<br/>Morristown, New Jersey 07960</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                   | 8. Performing Organization Rept. No.                    |                                |
| 12. Sponsoring Organization Name and Address<br><b>New Process Development Section<br/>Division of Process Control Engineering<br/>National Air Pollution Control Administration<br/>U. S. Department of Health, Education, and Welfare<br/>Washington, D. C.</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                   | 10. Project/Task/Work Unit No.                          |                                |
| 15. Supplementary Notes                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                   | 11. Contract/Grant No.<br><b>PH-22-68-24</b>            |                                |
| 16. Abstracts<br><p>Volume II of a two-volume report which summarizes the results and conclusions of a study of SO<sub>2</sub> reduction processes. This volume covers the Phase II activities of the study. Four of its five sections deal with experimental studies designed to optimize process conditions and to confirm the validity of assumptions made in Phase I studies. These sections cover (1) Claus Process Kinetics, (2) Intermediate Reactor studies, (3) Low temperature Claus Process studies, and (4) Strong SO<sub>2</sub> Reduction studies. The fifth section is a Phase I type study on the use of dimethylaniline to gather the SO<sub>2</sub> from smelter gases and deliver a concentrated SO<sub>2</sub> gas to a reduction process.</p> |                                   | 13. Type of Report & Period Covered<br><b>Final</b>     |                                |
| 14.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                   |                                                         |                                |
| 17. Key Words and Document Analysis. 17a. Descriptors<br><br>SO <sub>2</sub><br>Reduction (chemistry)<br>Flue gases<br>Kinetics<br>Mathematical model<br><br>17b. Identifiers/Open-Ended Terms<br><br>Claus Process<br><br>17c. COSATI Field/Group     ]3/B                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                   |                                                         |                                |
| 18. Availability Statement<br><br>Unlimited                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                   | 19. Security Class (This Report)<br><b>UNCLASSIFIED</b> | 21. No. of Pages<br><b>155</b> |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                   | 20. Security Class (This Page)<br><b>UNCLASSIFIED</b>   | 22. Price                      |

## FOREWORD

This two-volume report summarizes the results and conclusions made by the Industrial Chemicals Division of Allied Chemical Corporation for the National Air Pollution Control Administration under Contract No. PH-22-68-24.

Volume I covers Phase I activities performed between June 1, 1968 and July 31, 1969. The objective of Phase I was to establish the state-of-the-art of reduction to sulfur techniques. Based on a comprehensive literature survey, thirty case studies were worked up covering several types of sulfur oxide stack emissions and several reductants. Each case was based on the best information available, and use of updated technology in devising the process sequence. Flow sheets, operating parameters, and economics are reported in this volume.

Volume II covers Phase II activities performed between August 1, 1969 and September 30, 1970. Four of its five sections deal with experimental studies designed to optimize process conditions and to confirm the validity of assumptions made in the Phase I studies. These sections cover (1) Claus Process Kinetics, (2) Intermediate Reactor Studies, (3) Low Temperature Claus Process Studies, and (4) Strong SO<sub>2</sub> Reduction Studies. The fifth section is a Phase I type study on the use of dimethylaniline to gather the SO<sub>2</sub> from smelter gases and deliver a concentrated SO<sub>2</sub> gas to a reduction process.

The contract work reported herein covers an important approach to SO<sub>2</sub> pollution control. It shows the reduction to sulfur technique to be a viable vehicle. By establishing certain process applications to be either technically or economically untenable, it narrows the area to a few preferred routes. An example is the handling of smelter gas by a gathering process, with subsequent reduction of the concentrated SO<sub>2</sub> to sulfur. Laboratory investigations have optimized operating conditions for selected process steps, specifically the Intermediate Reactor and the Claus units, that are common to almost all reduction flow sheets.

Although many departments within the Allied Chemical complex contributed to this work, Industrial Chemicals Division's R & D staff held prime responsibility for its planning, direction, and completion. The following individuals had major time participation in this effort: Mr. C. A. Bernales, Intermediate Reactor and Strong Gas Studies in Phase II; Mr. S. B. Boucher, engineering support in Phase I; Mr. R. L. Burrell, Low Temperature Claus Studies in Phase II;

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(Continued)

Mr. R. H. Edgecomb, process engineering in Phase I; Mr. G. B. Falk, economic evaluations in Phases I and II; Mr. T. S. Harrer, engineering support in Phase I; Mr. R. S. Park, process engineering in Phases I and II; Dr. L. P. Sharma, general consultant and Strong Gas Studies in Phase II; Mr. R. L. Sturtevant, general consultant in Phase II; Dr. S. N. Subbanna, Claus Kinetic Studies in Phase II; and Mr. A. W. Yodis, Project Director of Phases I and II.

The cooperation of our NAPCA Project Officer, Mr. G. L. Huffman, is especially appreciated.

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1. CLAUS PROCESS KINETICS

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## 1.1 INTRODUCTION

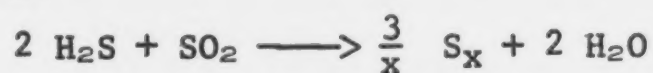
1.1.1 In recent years the emission of sulfur dioxide into the atmosphere has increased appreciably and is posing a serious air pollution problem. Reduction of  $\text{SO}_2$  to elemental sulfur is one useful approach to the abatement of sulfur dioxide atmospheric pollution.

1.1.2 Since June 1968, Allied Chemical Corporation has contracted with National Air Pollution Control Administration under Contract No. PH 22-68-24 to study the applicability of reduction to sulfur techniques to the development of new processes for removing  $\text{SO}_2$  from flue gases. The whole program was divided into three phases:

- Phase I - A comprehensive literature survey to select and evaluate potentially useful techniques.
- Phase II - Laboratory experimental work to generate knowledge or data not available in the literature, to test the assumptions on which Phase I evaluations rest and to develop or optimize selected reduction processes.
- Phase III - An engineering and economic study of processes surviving Phases I and II which is sufficiently detailed to allow a decision on further development leading to commercialization.

This report deals with the conventional (Normal) Claus and is a part of the Phase II effort.

1.1.3 The Claus process was developed in Germany in 1890. It consists of the vapor phase catalytic oxidation of hydrogen sulfide to elemental sulfur by reaction with sulfur dioxide.



The reaction takes place over an alumina catalyst at temperatures in the range of 392 to 752°F. Although the Claus process has been used commercially for many years, the literature provides no reliable kinetic data to permit optimum Claus reactor design. Reliable kinetic data are also needed to increase Claus reaction efficiency.



1.1.4 Substantially all  $\text{SO}_2$  reduction processes reported in the literature use the Claus process in the final stage of sulfur recovery. Therefore the efficiency of Claus operation has some effect on the overall sulfur recovery. The Claus process may be considered as the primary tool for reducing  $\text{SO}_2$  emissions to the atmosphere. In most cases the exhaust gases from the Claus unit are discharged into the atmosphere creating  $\text{SO}_2$  pollution problem. Therefore an increase in Claus reaction efficiency has the beneficial effect of reducing the  $\text{SO}_2$  atmospheric pollution.

1.1.5 Depending on the upstream reduction steps, the Claus feed may contain any or all of the following:  $\text{S}_2$ ,  $\text{CO}$ ,  $\text{COS}$ ,  $\text{CS}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in addition to the primary reactants  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . How these components behave under conditions optimal for  $\text{H}_2\text{S}/\text{SO}_2$  reaction can have a marked effect on sulfur yield. The question arises whether or not the  $\text{CO}$ ,  $\text{COS}$ ,  $\text{CS}_2$  and  $\text{H}_2$  react fully in the Claus unit in the residence time provided. If these reactions with  $\text{SO}_2$  are slower than the  $\text{H}_2\text{S}$  reaction, then either a large catalyst charge must be provided in the unit or loss of reductant be accepted. Either of these alternates would involve an economic penalty. It is not possible to answer any of these questions from the previously existing kinetic data. Incomplete conversion of  $\text{CO}$ ,  $\text{COS}$ ,  $\text{CS}_2$  and  $\text{H}_2$  in the Claus unit means incomplete utilization of the full reducing power of the upstream reductant. This results in increased cost of the upstream reductant. Depending on the composition of  $\text{CO}$ ,  $\text{COS}$ ,  $\text{CS}_2$  and  $\text{H}_2$  in the feed gases and the economics of the overall situation, it is necessary to decide whether or not an Intermediate Reactor is needed. The main purpose of the Intermediate Reactor is to completely react the components such as  $\text{CO}$ ,  $\text{COS}$ ,  $\text{CS}_2$  and  $\text{H}_2$  with  $\text{SO}_2$  and to ensure that  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and  $\text{S}_2$  are the only sulfur bearing species entering the Claus unit. Again no decision on the Intermediate Reactor can be taken with the available kinetic data.

1.1.6 It was therefore the aim of this program to develop a mathematical model for the kinetics of the Claus process. A further objective of this study was to determine the reactivity of  $\text{CO}$ ,  $\text{COS}$  and  $\text{H}_2$  in the feed gases. Depending on the reactivity of  $\text{CO}$ ,  $\text{COS}$  and  $\text{H}_2$  in the Claus unit, it was also the aim of this study to provide data which would allow decision as to whether or not an Intermediate reactor is needed. It was not the aim of this program to go into details of the mechanism of reaction which is a much more complicated problem than the development of a satisfactory rate equation.

## 1.2 SUMMARY

1.2.1 This report covers the development of a mathematical model for the kinetics of the normal temperature Claus process.

1.2.2 Experiments were carried out for generating the experimental kinetic data. These data were collected using the dynamic flow system over Porocel LPD catalyst. The temperature range was 400 to 700°F and the contact times were varied from 1/16 to 2.5 seconds. The H<sub>2</sub>S concentrations in the feed were varied from 1 to 6 percent. The experimental kinetic data for the Claus reactions are presented in Exhibits 1-5 through 1-18.

1.2.3 It was found that the reaction between H<sub>2</sub>S and SO<sub>2</sub> is very fast and reaches almost equilibrium conditions in 1/2 second contact time. The kinetics and the rate of (H<sub>2</sub>S + SO<sub>2</sub>) reaction is not affected by 20% water in the feed. For each temperature in the Claus range, there is an upper limit to the inlet compositions of H<sub>2</sub>S and SO<sub>2</sub>, above which, liquid sulfur condenses and deactivates the catalyst. Hence the Claus reactor must be operated above the dew point of sulfur. In general it may be said that (COS + H<sub>2</sub>O) and (COS + SO<sub>2</sub>) reactions are very slow compared to the (H<sub>2</sub>S + SO<sub>2</sub>) reaction. A substantial part of COS does react. Carbon monoxide reacts only to a slight extent even at 700°F. Hydrogen does not react at all and passes through like an inert. It is therefore concluded that in order to completely react the CO, COS and H<sub>2</sub> in the feed, it is necessary to employ an Intermediate Reactor.

1.2.4 The integral method was employed for analysis of kinetic data. The equations for each of the sub-systems were written and analog programs used to evaluate the rate constants. The overall model was built up stepwise with an effort made to use the least number of reactions. The final model was built using 8 reactions. The overall model is a digital program written in Fortran IV. It includes the complex equilibrium program to make certain that equilibrium conditions are ultimately reached at infinite contact time. For a given feed composition and temperature, the program goes through the complex equilibrium calculations as well as the Runge-Kutta numerical integration and prints out the product compositions as a function of contact time. The listing of the main program and computer printouts are given in Exhibits 1-30 and 1-31 respectively.

1.2.5 The model predicts the product distribution reliably over the normal Claus temperature range. At higher temperatures of 700°F, the conversions predicted by the model are less than those obtained by experiment. The experimental results at 700°F are considered unrealistic since the experimental conversions are even better than what the equilibrium permits. More than equilibrium conversions in these experiments are explained on the basis that further reaction must be taking place at lower temperatures (where equilibrium is more favorable) in the bottom leg of the reactor. Such a situation does not exist for lower temperature runs since the catalyst temperature and the bottom leg temperature are approximately the same.

1.2.6 The results predicted by the model are conditioned by the equilibrium considerations and therefore are quite safe for design purposes. Although the model is built using 1 to 6% H<sub>2</sub>S, it is expected on the basis of a few runs made, to hold good for at least 10% H<sub>2</sub>S in the feed.

1.2.7 It was found that CO<sub>2</sub>/H<sub>2</sub>S ratio has no effect on the conversion of H<sub>2</sub>S for CO<sub>2</sub> concentrations of 5 to 20% in the feed gases.

### 1.3 CONCLUSIONS AND RECOMMENDATIONS

1.3.1 It was found that the (H<sub>2</sub>S + SO<sub>2</sub>) reaction is very fast and reaches almost equilibrium conditions in 1/2 second contact time. Although some runs have been made in this work at very short contact times of 1/16, 1/8 and 1/4 seconds, further more detailed experimental work would be needed to define exactly the kinetics of this reaction at very short contact times. These experiments should be performed in a 1" reactor tube rather than in a 2" reactor tube used in this work. Using these more accurate kinetic data, the model can be improved and refined further.

1.3.2 The kinetics and the rate of (H<sub>2</sub>S + SO<sub>2</sub>) reaction was found to be unaffected by 20% water in the feed. The (COS + SO<sub>2</sub>), (COS + H<sub>2</sub>O) and (CO + SO<sub>2</sub>) reactions are very slow compared to the (H<sub>2</sub>S + SO<sub>2</sub>) reaction.

1.3.3 It is concluded that in order to completely react CO, COS and H<sub>2</sub>, it is necessary to employ an Intermediate Reactor. The Intermediate Reactor may be recommended for any particular reduction scheme, depending on the composition COS, CO and H<sub>2</sub> in the feed, the overall economics and the atmospheric pollution problem.



1.3.4 All work in this study was done by employing Porocel LPD catalyst. The conclusions drawn are therefore true only for this catalyst. A catalyst development program may possibly uncover another catalyst that would enhance the reactivity of less reactive constituents.

1.3.5 The model predicts the product compositions reliably over the Claus temperature range. The conversions predicted by the model are less than those obtained by the experiment around 700°F. However, the experimental results are considered unrealistic at these higher temperatures. The use of the model is quite safe for design purposes even at 700°F. The model is conditioned by the equilibrium considerations.

1.3.6 It is recommended that more accurate kinetic data be collected at 700°F before attempting to improve the model. Improvements in the experimental apparatus and sampling techniques should be incorporated for avoiding the further reaction in the bottom leg of reactor. The exit samples should be taken immediately after the catalyst bed to eliminate any chance for further reaction.

1.3.7 The model is built up using 1 to 6% H<sub>2</sub>S in the feed. It is expected, on the basis of the few runs made, to hold good for 10% H<sub>2</sub>S in the feed. Since the model is semi-empirical, the extrapolation beyond the range of variables tested may or may not be good.

1.3.8 The model is built considering only S<sub>8</sub> as the elemental sulfur species. This is a good approximation in the Claus temperature range. However, at 700°F other forms of sulfur species such as S<sub>2</sub>, S<sub>4</sub> and S<sub>6</sub> are also present to some extent. The model could be improved by considering these species although the model would become complicated. No such attempt was made in this study.

1.3.9 From the point of view of kinetics, 1/2 second contact time for (H<sub>2</sub>S + SO<sub>2</sub>) reaction is sufficient. However the contact time to be used in any real situation also depends on the overall optimal operation of the plant and the SO<sub>2</sub> atmospheric pollution considerations.

#### 1.4 BACKGROUND (PRIOR ART)

1.4.1 The demonstration of the rapid reaction between hydrogen sulfide and sulfur dioxide in the presence of moisture was a common lecture experiment as early as 1812, but it is not known by whom this reaction was first

observed. However Chuzel (1) in 1812 noted that no reaction would result between hydrogen sulfide and sulfur dioxide if the gases were first dried by passing over calcium chloride.

1.4.2 Matthews (2) in 1926 confirmed that dry gaseous  $\text{H}_2\text{S}$  and  $\text{SO}_2$  do not react on mixing but they will react in the presence of a liquid film of water on exposed surfaces. He did not carry out any quantitative experiments on  $\text{H}_2\text{S}/\text{SO}_2$  reaction.

1.4.3 Lidov (3) in 1928 noted that the reaction between  $\text{H}_2\text{S}$  and  $\text{SO}_2$  is very rapid and complete. He even suggested that  $\text{H}_2\text{S}$  may be determined by adding a known amount of  $\text{SO}_2$ .

1.4.4 Randall and Bichowsky (4) in 1918 showed that the rate of reaction between  $\text{SO}_2$  and  $\text{H}_2\text{S}$  depends on the surface of the reaction vessel. They observed that a very small amount of sulfur is formed when a mixture of moist  $\text{SO}_2$  and  $\text{H}_2\text{S}$  is passed through a clean glass tube at  $60^\circ\text{C}$ , but if the tube is first etched, then the sulfur is formed at a more rapid rate.

1.4.5 Taylor and Wesley (1) in 1926 studied the kinetics of the gaseous reaction between  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . They used the dynamic flow method and the reactions were conducted in glass tubes. The gases after reaction were cooled rapidly to  $100^\circ\text{C}$ , where the reaction rate is exceedingly slow. The unreacted  $\text{H}_2\text{S}$  and  $\text{SO}_2$  were analyzed by absorbing them in  $\text{NaOH}$  solutions. They covered a temperature range of  $371$  to  $733^\circ\text{C}$  in two reaction tubes of the same volume but with different surface areas ( $317$  and  $121\text{ cm}^2$ ). They found that the reaction rate is determined by the equation

$$S = k P_{\text{H}_2\text{S}}^{1.5} P_{\text{SO}_2}$$

where  $S$  is the amount of sulfur formed in gms/min.

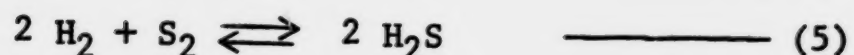
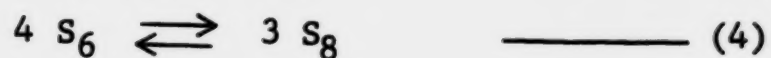
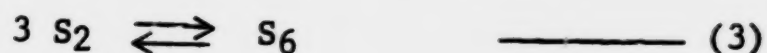
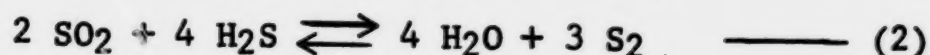
$k$  is the rate constant.

$P_{\text{H}_2\text{S}}$  and  $P_{\text{SO}_2}$  are the average partial pressures of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  respectively.

They finally concluded that the reaction rate between  $\text{H}_2\text{S}$  and  $\text{SO}_2$  is proportional to the surface area of the reaction vessel. The reaction takes place almost exclusively on the surface of the reaction vessel and very little in the gaseous phase.



1.4.6 Yushkevich et al (5) in 1932 made equilibrium calculations for  $\text{H}_2\text{S}$  and  $\text{SO}_2$  reaction for the temperature range of 200 to 800°C and pressure range of 5 to 760 mm Hg, on the basis of the following reactions:



However the reaction (5) may be ignored for equilibrium calculations below 700°C because of the formation of negligible amounts of  $\text{H}_2$ . Above 900°C where  $\text{S}_2$  molecules predominate, the reaction (2) is endothermic. Therefore from reaction (2) alone, one would expect that the higher the temperature, the more complete the reaction between  $\text{SO}_2$  and  $\text{H}_2\text{S}$ . If reactions (2), (3), (4), and (5) are considered simultaneously, the equilibrium conditions change markedly.

1.4.7 Yushkevich et al (5) found that the  $\text{H}_2\text{S}$  and  $\text{SO}_2$  reaction is very slow in the absence of a catalyst. They used catalysts such as Tikhvinsk bauxite ( $\text{SiO}_2:\text{Fe}_2\text{O}_3:\text{Al}_2\text{O}_3::8.5:20.4:61.0$ ), Alapaevsk bauxite ( $\text{SiO}_2:\text{Fe}_2\text{O}_3:\text{Al}_2\text{O}_3::4.5:26.5:27.2$ ) and Alapaevsk iron ore ( $\text{Fe}_2\text{O}_3:\text{Al}_2\text{O}_3:\text{SiO}_2::80.0:14.1:4.0$ ). While using bauxite catalysts they observed that at 100°C and SVH of 120-130, the reaction practically goes to completion (98-99%) and both types of bauxites are equally good. However their experiments indicate a decrease in the degree of reaction for dilute gases ( $\text{H}_2\text{S}:\text{SO}_2::1.5:0.75$ ) and rapid decrease in reaction rate for temperatures below 100°C. They also found that at 200°C and SVH of 1000, the reaction was completed to 86% with bauxitic iron ore catalyst while Tikhvinsk bauxite gave only 24% conversion of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  ( $\text{H}_2\text{S}:\text{SO}_2:\text{N}_2::1.5:0.75:97.75$ ) at the same temperature and SVH of 725. They finally concluded that the bauxite iron ore catalyst is better than the bauxite catalysts.

1.4.8 Lepsoe (6) in 1940 studied the kinetics of  $\text{SO}_2$  reduction by carbon, CO and COS. He found that the reduction of sulfur dioxide by carbon may be expressed satisfactorily by the following consecutive reactions



The rate of formation of  $\text{CO}_2$  between  $900^\circ\text{C}$  and  $1200^\circ\text{C}$ , expressed as moles in the reaction products, is given by the formula

$$(\text{CO}_2) = 1.11[(\text{SO}_2) - (\text{SO}_2)^{0.1}]$$

He observed that above  $1200^\circ\text{C}$ , the rate of sulfur dioxide reduction appears to be controlled by gas diffusion rates and substantially the same depth of fuel bed being required for the reduction of  $\text{SO}_2$ , regardless of gas velocity. He also found that the reduction of sulfur dioxide by means of  $\text{CO}$  or  $\text{COS}$  is very fast with any kind of catalyzing surface above  $800^\circ\text{C}$ . At lower temperatures ( $250$  to  $500^\circ\text{C}$ ) alumina is an efficient catalyst and the reaction appears to be of the first order. His experiments show that the reduction with  $\text{COS}$  is approximately four times as fast as with carbon monoxide. He used SVH of 60 and reports reaction efficiency of 80 to 100% for  $\text{COS}/\text{SO}_2$ .

1.4.9 Gamson and Elkins (7) in 1953 presented a review of literature on the conversion of  $\text{H}_2\text{S}$  to elemental sulfur. In this article, the thermodynamics of the formation of sulfur from hydrogen sulfide is developed and a rigorous and unique calculation procedure is outlined. They have made equilibrium calculations for  $\text{H}_2\text{S}/\text{O}_2$  and  $\text{H}_2\text{S}/\text{SO}_2$  reactions. They give kinetic and yield data for the reaction of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  covering superficial space velocities of 240 to 1920 SVH, and temperatures from  $230$  to  $300^\circ\text{C}$ . They give similar data for the reaction of  $\text{COS}$  and  $\text{SO}_2$ , using an SVH fixed at 200 and varying the temperature from  $222$  to  $303^\circ\text{C}$ . Their results show that for a feed gas of 5.5%  $\text{COS}$ , 2.75%  $\text{SO}_2$ , and 91.75%  $\text{N}_2$ , the reaction is 97.2% complete at a temperature of  $303^\circ\text{C}$ . They used the dynamic flow method and 4-8 mesh Porocel catalyst.

1.4.10 For the  $\text{COS}-\text{SO}_2$  reaction, superficial space velocity (SVH) used by Lepsoe is 60 and that used by Gamson and Elkins is 200. Both of these are low and do not cover the full range of typical normal Claus operation.

1.4.11 Munro and Masdin (8) in 1967 studied the desulfurizing of fuel gases. Their equilibrium calculations for  $\text{H}_2\text{S}$  and  $\text{SO}_2$  reaction were in agreement with those of Gamson and Elkins discussed before. They used 13X molecular sieve as catalyst in their experimentation. They found good agreement between experimental results and theoretical predictions. They therefore concluded that the theory can be used to predice accurately the conversion when using a fully active catalyst.

1.4.12 On the basis of the existing kinetic data, one cannot accurately predict the behavior of  $\text{COS}$  in the Claus regime under the usual operating conditions, although it is clearly evident that  $\text{H}_2\text{S}$  is more reactive than  $\text{COS}$ . Kinetic data for  $\text{COS}$  reactivity has been developed covering a wider range of parameters.

1.4.13 The discussion so far was an attempt to survey the existing literature on the kinetics of Claus process. It is by no means complete. However, one must conclude that although the Claus process has been used commercially for many years the literature provides no reliable kinetic data to permit optimum Claus reactor design.

## 1.5 THEORY

1.5.1 The main objective of this program was to find an adequate rate equation for the kinetics of the Claus reaction. At present chemical kinetics is not, however, an exact science. From a practical standpoint it is not yet possible to formulate generalized mathematical relations for the rate of a chemical reaction. It is, therefore, necessary to determine the rate of reaction experimentally.

1.5.2 Kinetic data for a catalytic system are best obtained in flow reactors and the method most often used is the integral reactor. Integral reactors have a distinct advantage over differential reactors because the chemical analysis need not be very rigorous for a reasonable degree of accuracy. The compositions are measured as a function of feed rate and temperature. Kinetic data obtained in this manner are the most dependable and simple to use. The method has the advantage of direct applicability to flow-type reactors.

1.5.3 The Claus reactions are heterogeneous vapor phase catalytic reactions. It is assumed that the reaction proceeds at all the gas-solid interfaces both at the outside boundaries and within the porous catalyst pellets. For such a reaction we select, as the most reasonable representation of reality, a continuous-reaction model which pictures reaction occurring to a lesser or greater extent throughout the catalyst pellets. This is in contrast to the shrinking unreacted-core model with its definite zone of reaction which most reasonably represents the real case in the majority of non-catalyzed gas-solid reactions.

1.5.4 In developing rate expressions for the continuous reaction model, the various processes that may cause resistance to reaction must be taken into account. These are:

(a) Gas Film Resistance - Reactants must diffuse from the main body of the gas to the exterior surface of the catalyst.



(b) Pore Diffusion Resistance - Substantially all of the surface area of the catalyst is inside the pores. Therefore the reactants must in general move into the pellet through the pores.

(c) Surface Phenomenon Resistance - The reactants are adsorbed to the surface of the catalyst where they react to give products. The products are then desorbed back to the gas phase within the pore.

(d) Pore Diffusion Resistance for Products - Products then diffuse out of the pellet.

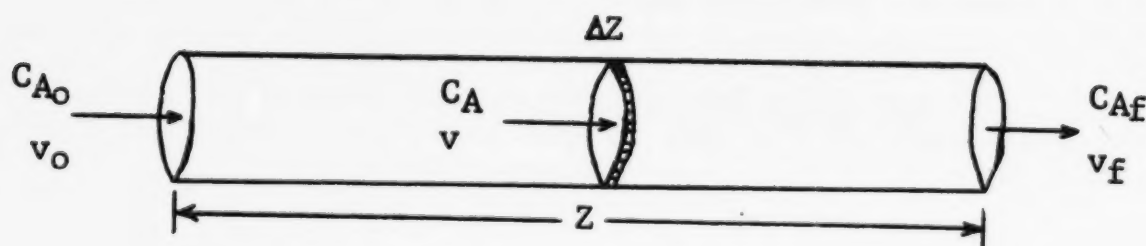
(e) Gas Film Resistance for Products - Products then move from the mouth of pores to the main gas stream.

1.5.5 Since the steps listed above take place in series, it is possible for any one of them to control the overall rate of reaction. The slowest step is known as the rate controlling step. The experimental data were collected to obtain a reliable rate equation for Claus reactions. Therefore, proper precautions were taken to make certain the step (c) is the rate controlling step.

1.5.6 The effects of diffusional resistance are kept to a minimum by using a high velocity through the catalyst bed. These effects may be tested for in the experimental reactor by varying the weight of catalyst and the feed rate (W/F) at the same time (9). The conversion is measured at a value of W/F at which the gas velocity is low. Then it is measured again at a high velocity, but with more catalyst to keep the ratio W/F constant. The values of conversion will coincide if the effects of diffusion is negligible. If the conversions are different, there is a diffusional effect. The experimental kinetic data and the conversions, obtained at different linear velocities, but at same W/F values are shown in Exhibit No. 1-1. It may be seen that the conversions are approximately the same within experimental error.

1.5.7 The following paragraphs discuss rate of reactions.

In contrast to the batch case, consider the system where the reactants flow continuously into the reactor and the products are continuously removed. The flow reactor may be represented by the figure given below.





$C_A$  is the concentration of substance A in moles/ft<sup>3</sup> and  $v$  is the volumetric flow rate in ft<sup>3</sup>/hour. The subscripts o and f indicate the entrance and outlet conditions.

The material balance for a reaction component A may be made for a differential element of length  $\Delta Z$ .

Input-Output-Disappearance by Reaction = Accumulation

$$(vC_A)|_Z - (vC_A)|_{Z+\Delta Z} - (kC_A)S\Delta Z = \frac{\partial}{\partial t} (S\Delta Z C_A) \quad (1)$$

It is assumed that the heterogeneous catalytic reaction takes place with apparent first order with respect to component A for purposes of illustration. In the above equation  $S$  is the void cross-section of the tube and  $k$  is the reaction rate constant. The partial differential equation then becomes

$$- \frac{\partial}{\partial Z} (vC_A) - kC_AS = S \frac{\partial C_A}{\partial t} \quad (2)$$

At steady state

$$\frac{\partial C_A}{\partial t} = 0$$

$$\therefore \frac{d}{dZ} (vC_A) = -kC_AS \quad (3)$$

1.5.8 In the Claus reactions studied in this program, about 90 percent of flow rate is due to inert nitrogen gas. The change in the volumetric flow rate due to change of moles by reaction is negligible. Therefore  $v$  may be considered as constant.

$$\therefore v \frac{dC_A}{dZ} = -kC_AS \quad (4)$$

The contact time  $\tau$  is defined by

$$\tau = \frac{V_r}{v} \quad (5)$$

where  $V_r$  is the void volume of the reactor.

From equations (4) and (5), it follows that

$$\frac{dC_A}{d\tau} = -kC_A \quad (6)$$

Under the conditions and assumptions described above, equation (6) gives the desired rate expression.

1.5.9 In the past chemical engineers have frequently used the Langmuir-Hinshelwood approach, which provides the adsorption terms for correlating the kinetic data for heterogeneous reactions. This approach does not have the theoretical validity commonly attributed to it and its use leads to unnecessary mathematical complexity. It seems reasonable that the simplest possible rate equation which will adequately fit the experimental data be employed. The following expression for the rate equations is among the simplest forms having sufficient generality (10).

$$\text{rate} = k(p_A)^m(p_B)^n(p_C)^o \text{ --- (7)}$$

Where A and B might be reactants and C a product or a foreign gas. Depending on the accuracy of the experimental data, the exponents m, n and o may or may not be restricted to integral or half-integral values. The exponents in the above equation may be considered as simply the apparent orders of the reaction with respect to the individual components.

## 1.6 LABORATORY EXPERIMENTAL WORK

### 1.6.1 Apparatus

1.6.1.1 The main aim of the experimental work was to generate the kinetic data needed for developing the rate equation. A schematic diagram of the experimental apparatus used is shown in Exhibit No. 1-2. It consists of a 2" reactor where the reactions are carried out with necessary auxiliary equipment.

1.6.1.2 The reaction gases were metered using Fischer-Porter rotameters and mixed with metered gaseous  $N_2$  so as to obtain the required reactant gas concentrations. Where desired  $H_2O$  was introduced into the gas stream by bubbling the  $N_2$  flow through a thermostated water saturator. The reaction gases were manifolded and passed downward through the vertical 2" I.C. Vycor reactor tube containing 10" of the catalyst bed. The reaction temperatures were maintained by a Lindberg Heviduty 3-Zone tube furnace. All three zones were equipped with separate Pyrovane temperature controllers. The controllers were adjusted to obtain essentially a flat temperature profile. Typical temperature profiles under actual run conditions are shown in Exhibits 1-3 and 1-4.

1.6.1.3 After leaving the reactor, the exit gases were passed through the bottom leg of the reactor (Pyrex U-tube), which was maintained around  $375^\circ F$  to prevent sulfur blockage. Before the reaction products

were vented to the exhaust hood system, they were sampled and analyzed by gas chromatographic techniques for  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}$ ,  $\text{COS}$ ,  $\text{CS}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , etc., as appropriate for the system under study. Provisions were also incorporated for sampling of the inlet gas stream and, where appropriate, such samples were taken and similarly analyzed using the gas chromatographic techniques.

#### 1.6.2 Experimental Procedure

1.6.2.1 The required depth of the catalyst bed was added to the reactor tube. Reactant gases of the required composition were passed through the reactor by adjusting the rotameters of the various gases. Temperature controllers were turned on to bring the reactor to the required temperature. In the beginning the water saturator was by-passed and dry  $\text{N}_2$  was mixed with other reactant gases. Two feed samples were taken without using any drying tube since the gases were already dry. After taking feed samples, if required,  $\text{N}_2$  was passed through the water saturator. The temperature of water saturator was adjusted to give the percent water required in the reactant gases.

1.6.2.2 The temperatures at various heights in the catalyst bed were measured and the temperature controllers were adjusted to get essentially a flat temperature profile across the height of the catalyst bed. When  $\text{N}_2$  was passed through the water saturator, the line from the saturator to reactor was heated and maintained at a temperature slightly higher than the saturation temperature. This was necessary to avoid any water condensation from the saturated  $\text{N}_2$  stream. Heat was also supplied to the bottom leg where the temperature was maintained around  $375^\circ\text{F}$  to prevent any sulfur blockage.

1.6.2.3 The whole system was then allowed to reach steady state conditions. When everything was steady the exit samples were taken. The exit sampling device consisted of a calcium chloride drying tube and the sample bomb. The exit gas was first passed through the calcium chloride drying tube to remove sulfur and moisture and the dry sample was then collected in the sample bomb. For each run four exit samples were taken. In between samples, the temperature profile was measured to make certain that the experimental conditions had not changed.

1.6.2.4 After taking the exit samples, the water saturator was again by-passed and the dry  $\text{N}_2$  stream was mixed with dry reactant gases. Two more feed samples were taken. This was to check that gases had been flowing at steady rate without any fluctuations. The feed samples as well as exit samples were analyzed using two



column gas chromatography. In most cases, the samples were analyzed within one hour of collection. The samples containing air were discarded.

### 1.6.3 Experimental Data and Discussion of Results

1.6.3.1 Exhibits 1-5 through 1-18 present the experimental kinetic data as they were obtained from the G.C. analyses. These data were used during subsequent computer evaluations resulting in the determination of the reaction rate constants.

Depending on the particular system under study, experiments were performed from 400 to 700°F. Reactant gas concentrations were varied from 1 to 6 percent. The contact times were varied from 1/16 to 2.5 seconds. Contact times were calculated based on the reactor temperature and on the assumption of 50% voids in the catalyst bed. It may be given by

$$\text{Contact Time} = \frac{\text{Void volume of catalyst bed in cu. ft.}}{\text{Flow rate of feed gases at the reactor temperature and atmospheric pressure in cu. ft./sec.}}$$

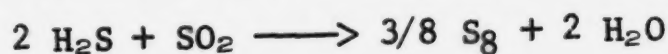
1.6.3.2 Experience has shown that while rotameters are accurate to within  $\pm 10\%$ , they are also subject to variations resulting from the slight changes in back pressure encountered in this work. The variations thus found in the inlet gas compositions were naturally reflected to some degree in similar variations in the exit gas analyses. Since all gas analyses were carried out using gas chromatographic techniques, they were subject to the errors inherent in this method. Since the G.C. nitrogen analysis was not reliable, it was impossible to obtain an accurate check on a 100% summation basis. Analytical methods did not lend themselves to direct determination of  $\text{H}_2\text{O}$  or sulfur. Where these constituents are present in the gases exiting the reactor, their concentrations could only be calculated by differential mass balance over the system. Little error in this technique was expected, since the inlet  $\text{H}_2\text{O}$  constant was based on the assumption that saturation was obtained at the controlled temperature of the water. This method of  $\text{H}_2\text{O}$  addition has been verified to be quite accurate.

1.6.3.3 All factors considered it is estimated that the experimental data are within  $\pm 10-15\%$  of the true values. This is further born out by comparison of the results of duplicate tests, run at different times. Analog evaluations of the experimental data further substantiated this conclusion, particularly when weighted consideration was given to values checked by duplicate runs.



### H<sub>2</sub>S + SO<sub>2</sub> + H<sub>2</sub>O

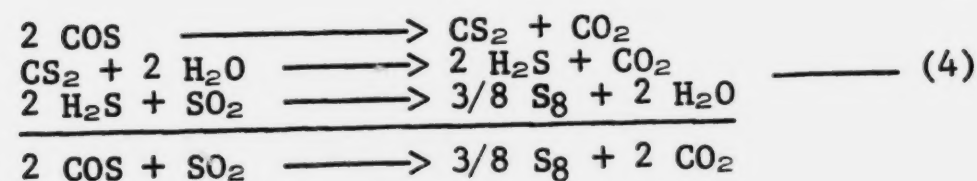
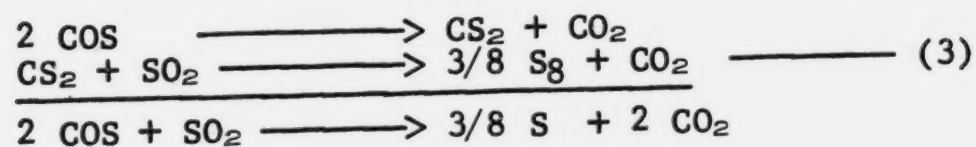
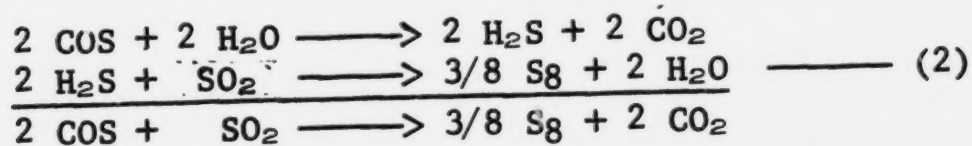
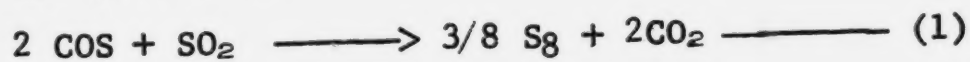
1.6.3.4 The experimental kinetic data for (H<sub>2</sub>S + SO<sub>2</sub>) and (H<sub>2</sub>S + SO<sub>2</sub> + H<sub>2</sub>O) are given in Exhibit 1-5 through 1-8. In general it was found that the (H<sub>2</sub>S + SO<sub>2</sub>) reaction is very fast and reaches almost equilibrium values in 1/2 second contact time. It was also found that the kinetics of (H<sub>2</sub>S + SO<sub>2</sub>) reaction is not affected by the presence of 20% water in the feed. It was observed that at 400 and 450°F, if the feed compositions of H<sub>2</sub>S and SO<sub>2</sub> are high, liquid sulfur condenses and deactivates the catalyst. A feed composition of 1.5% SO<sub>2</sub> and 3% H<sub>2</sub>S was used at 400 and 450°F. Even in these cases some liquid sulfur condensation were observed on the walls of the reactor but not on the catalyst. The following reaction was assumed for the kinetic analyses.

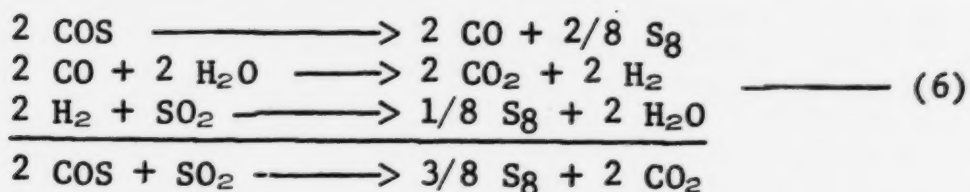
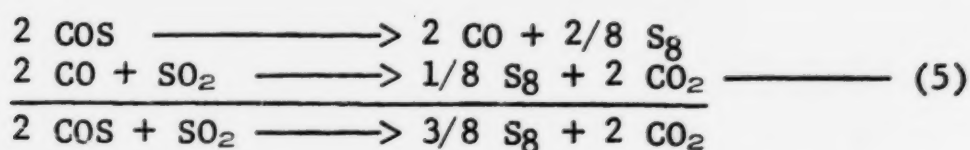


It was assumed that mainly S<sub>8</sub> is formed in the above reaction although some amounts of S<sub>4</sub> and S<sub>6</sub> are also simultaneously formed.

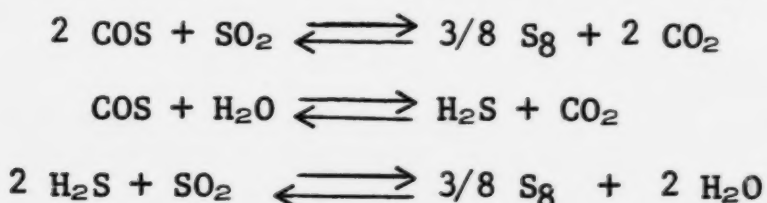
### COS + SO<sub>2</sub> + H<sub>2</sub>O

1.6.3.5 The experimental kinetic data for (COS + SO<sub>2</sub>), (COS + H<sub>2</sub>O) and (COS + SO<sub>2</sub> + H<sub>2</sub>O) are given in Exhibits 1-10 through 1-13 respectively. The following reactions are possible.





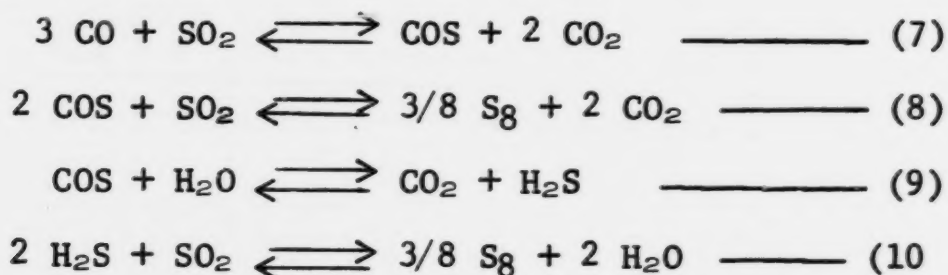
1.6.3.6 An examination of the kinetic data indicates that a substantial part of COS does react in the normal Claus and no CO is formed in the products. Hence there is no need to account for CO in the rate equation. Therefore possibilities (5) and (6) are eliminated. The experimental data also indicate that no CS<sub>2</sub> is formed. Even if COS is decomposing to form CS<sub>2</sub> and CO<sub>2</sub>, the CS<sub>2</sub> formed must be reacting completely leaving no CS<sub>2</sub> in the products. Therefore alternates (3) and (4) are the same as (1) and (2). For these reasons, the kinetics were developed based on the following reactions.



#### CO + SO<sub>2</sub> + H<sub>2</sub>O

1.6.3.7 The experimental kinetic data for (CO + SO<sub>2</sub> + H<sub>2</sub>O) and (CO + H<sub>2</sub>O) are reported in Exhibits 1-14 and 1-15 respectively. These data indicate that there is no reaction of carbon monoxide in the normal Claus range. However, there is some reaction at 600 and 700°F.

Carbon monoxide can react with SO<sub>2</sub> to form COS and CO<sub>2</sub>. The COS formed can react in many possible ways as discussed before. After considering these as well as other possibilities, it was found that the kinetics may be developed by the following reactions.



### H<sub>2</sub> + SO<sub>2</sub> + H<sub>2</sub>O

1.6.3.8 The experimental kinetic data are reported in Exhibit 1-9. Examination of the kinetic data indicates that there is hardly any reaction in the whole range of 400 to 700°F.

### Overall Reaction

1.6.3.9 In order to get an overall picture of the Claus process, experimental kinetic data on the overall reaction were obtained. Typical Claus feed conditions were used in these runs. Necessary care was taken to see that sufficient SO<sub>2</sub> was available to react completely H<sub>2</sub>S, CO, COS and H<sub>2</sub>. The experimental kinetic data are reported in Exhibit 1-16.

1.6.3.10 The results seem to be in order. These were expected on the basis of the individual reactions. It is expected that the overall kinetic model may be developed on the basis of reactions (7) through (10), given before. These data were later used to check the overall kinetic model.

### Condition of Catalyst after Run

1.6.3.11 The condition of catalyst was found good after (H<sub>2</sub>S + SO<sub>2</sub>), (H<sub>2</sub>S + SO<sub>2</sub> + H<sub>2</sub>O), (H<sub>2</sub> + SO<sub>2</sub> + H<sub>2</sub>O) and the overall reaction runs. But after (COS + SO<sub>2</sub>), (COS + H<sub>2</sub>O), (COS + SO<sub>2</sub> + H<sub>2</sub>O), (CO + H<sub>2</sub>O) and (CO + SO<sub>2</sub> + H<sub>2</sub>O) runs, it was found that catalyst had turned slightly dark. It is attributed that it was due to carbon deposition on the catalyst. However, no deactivation of the catalyst was observed. No catalyst life study was made.

### Reactivity of COS

1.6.3.12 In general it may be stated that a substantial part of the COS reacts in the Claus reactor. The extent of reaction of course depends on the temperature and contact time provided.

### Reactivity of CO

1.6.3.13 Although there is negligible reaction between CO and SO<sub>2</sub> up to 600°F, it is possible that CO may react with sulfur to form COS, which in turn could react with SO<sub>2</sub> to form sulfur. Since H<sub>2</sub>S and SO<sub>2</sub> react very rapidly, the sulfur vapor formed is available to test the reaction between CO and sulfur. Therefore a few runs of

( $\text{H}_2\text{S} + \text{SO}_2 + \text{CO}$ ) reaction were made. The results of these runs are reported in Exhibit No. 1-17. These data indicate that there is negligible reaction between CO and sulfur at 500°F.

#### Reactivity of $\text{H}_2$

1.6.3.14 There is hardly any reaction of  $\text{H}_2$  with any other constituent of Claus feed. Therefore it may be considered that  $\text{H}_2$  passes through Claus process as an inert.

#### Intermediate Reactor

1.6.3.15 Carbon monoxide does not react at less than 600°F. Even at 700°F, there is only partial reaction. There is no reaction of  $\text{H}_2$  in the range of 400-700°F. There is partial reaction of COS in the Claus temperature range. These results indicate the necessity of an Intermediate Reactor to completely react COS, CO and  $\text{H}_2$ . The actual use of an Intermediate Reactor depends on the quantity of COS, CO and  $\text{H}_2$  present in the feed and the overall economics of the situation.

#### Effect of $\text{CO}_2/\text{H}_2\text{S}$ Ratio

1.6.3.16 It has been reported in the literature (14) that the Claus reaction efficiency is affected by the  $\text{CO}_2/\text{H}_2\text{S}$  ratio in the feed gases. The ( $\text{H}_2\text{S} + \text{SO}_2 + \text{H}_2\text{O} + \text{CO}_2$ ) runs were made to test the effect of  $\text{CO}_2/\text{H}_2\text{S}$  ratio on the Claus reaction efficiency. The experimental results are reported in Exhibit No. 1-18. The concentration of  $\text{CO}_2$  was varied from 5% to 20% in the feed gases. The results indicate that  $\text{CO}_2/\text{H}_2\text{S}$  ratio has no effect on the conversion of  $\text{H}_2\text{S}$  at 500°F and 1 second contact time in the range tested.

### 1.7 THE KINETIC MODEL

#### 1.7.1 General

1.7.1.1 At present the quantitative treatment of reaction rates rests largely on an empirical basis, especially for the majority of industrially important reactions. The interpretation of experimental data and kinetic analysis is in most cases an individual problem.



1.7.1.2 The main objective of this program was to develop a mathematical model for the rate of the Claus reactions. It was not the purpose of this program to go into details of the mechanism of the reaction. The evaluation of the mechanism of a reaction is a much more complicated problem than the development of a satisfactory rate equation. The rate equation may be developed from a knowledge of the overall reaction and the exact sequence of steps involved in the reaction need not be known. Therefore stepwise reactions to produce intermediates were largely ignored except where the intermediates were detected.

1.7.1.3 For practical reasons it was desirable to find the simplest model which adequately simulated the laboratory data over the range of variables. Chemical kinetics calls for increasing or decreasing the order of a reactant in the equations, depending upon the stoichiometry or mechanism. In practice a workable mathematical model can be developed by using equations that are first order in each reactant in a majority of the problems encountered. This is especially true if the number of equations is large, since the nonlinearity, which may be necessary to fit the data, is obtained from the large number of terms. For this reason the model is partially empirical, but an effort was made to incorporate mechanistic terms so that when variables are manipulated the computer system will respond in the same manner as the real system. Use of this type of approach is justified by the time saved and its simplicity.

1.7.1.4 An effort was also made to abide by theoretical considerations such as maintaining the proper ratio of rate constants in a reversible reaction and obtaining a straight line for the Arrhenius plot.

When a number of reactions take place simultaneously as in the Claus process, each reaction may be assumed to take place at its own specific rate independent of the others and to follow the simple reaction rate equation. The overall rate equation may then be considered as the summation of the rates of all the independent reactions taking place. The general procedure then consisted of setting up simple differential-rate equations of the proper order for each separate reaction in terms of disappearance of reactants and the rate of formation of products and then to combine them to get the overall rate.

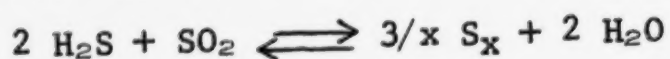
1.7.1.5 The rate constants and the order of reactions were determined by matching the theoretical predictions with experimental data on an analog computer. An assumed rate equation was integrated on an analog computer to give a relationship between concentration and time. This theoretical relationship was then compared with the experimental concentration vs. time data to find the  $k$  (rate constant) and the order of reaction.

1.7.1.6 The search for the values of the rate constants involved repeated fitting of the data. Once the best fit to data was obtained at three or more temperatures, the values of the rate constants were plotted as  $\log k$  vs.  $1/T$ . If a straight line or a reasonable facsimile was not obtained, computer runs were again made and new values obtained, still maintaining a reasonable fit to the data with perhaps some of the deviations from the data now in the opposite direction. A new Arrhenius plot was drawn and compared with the previous plot. New straight lines were drawn using all the points from both trials and the values obtained again rechecked against the data. By knowing the rate constants at several temperatures, the activation energy and temperature dependence of rate were established. The effects of diffusional resistance were kept to a minimum by using a high velocity through the catalyst bed.

1.7.1.7 The overall model was built up stepwise with an effort made to use the least number of reactions. The free energy of the reactions and their equilibrium constants were calculated from values found in the latest JANAF tables (11). Exhibit No. 1-19 lists the values of the equilibrium constants at four temperatures.

1.7.1.8 Another consideration was the relative rates of the reactions. If a reaction rate constant had a value 10,000 times smaller than the fastest reaction at any particular temperature, it was ignored, unless it was involved in a rate controlling step or required to give correct equilibrium concentrations.

1.7.1.9 The Claus reaction may be written as:



The reaction takes place over an alumina catalyst at temperatures in the range of 392 to 752°F. In the above reaction  $\text{S}_x$  is a mixture of the gaseous sulfur species  $\text{S}_2$ ,  $\text{S}_4$ ,  $\text{S}_6$  and  $\text{S}_8$ . Below 1650°F, there exists a complicated equilibrium system between the four species of gaseous sulfur, which is dependent upon the temperature and the total sulfur vapor pressure. In the normal temperature Claus range  $\text{S}_8$  is the most stable and predominant form of sulfur. It was therefore assumed in this work that gaseous sulfur exists only as  $\text{S}_8$ .

1.7.1.10 Contact times were calculated based on the reactor temperature and on the assumption of 50% voids in the catalyst bed. It is given by

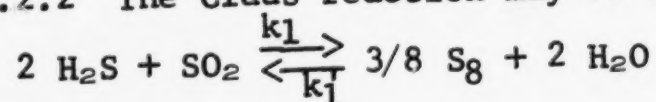
$$\text{Contact Time (sec.)} = \frac{\text{Void volume of catalyst bed in cu. ft.}}{\text{Flow rate of feed gases at the reactor temperature and atmospheric pressure in cu. ft./sec.}}$$

## 1.7.2 Sub-Systems

1.7.2.1 This section deals with the method of evaluating the rate constants. Kinetic rate equations for each of the sub-systems were written and analog programs used to evaluate the rate constants. All the analog programs were solved on an Electronic Associates Inc. TR-48 analog computer. An effort was made to abide by the theoretical consideration of obtaining a straight line for the Arrhenius plot. Only the forward rate constants could be determined with any degree of accuracy on the analog computer. The reverse rate constants were later determined and incorporated in the overall kinetic model.

### H<sub>2</sub>S + SO<sub>2</sub>

1.7.2.2 The Claus reaction may be represented by



In the above reaction  $k_1$  is the forward rate constant and  $k_1'$  is the reverse rate constant. The rate constants are referred to the sulfur dioxide component. It was assumed that only  $\text{S}_8$  is formed in the above reaction. Both the forward and reverse reactions were considered although only the forward rate constant was determined on the analog computer. The scaled equations programmed on the analog computer were:

$$-\frac{d}{dt}[2.5 \text{SO}_2] = 0.8 k_1[2.5 \text{SO}_2][1.25 \text{H}_2\text{S}] - 1.6 k_1'[5 \text{S}_8][0.3125 \text{H}_2\text{O}]$$

$$-\frac{d}{dt}[1.25 \text{H}_2\text{S}] = 0.8 k_1[2.5 \text{SO}_2][1.25 \text{H}_2\text{S}] - 1.6 k_1'[5 \text{S}_8][0.3125 \text{H}_2\text{O}]$$

$$-\frac{d}{dt}[5 \text{S}_8] = -0.6 k_1[2.5 \text{SO}_2][1.25 \text{H}_2\text{S}] + 1.2 k_1'[5 \text{S}_8][0.3125 \text{H}_2\text{O}]$$

$$-\frac{d}{dt}[0.3125 \text{H}_2\text{O}] = -0.2 k_1[1.25 \text{H}_2\text{S}][2.5 \text{SO}_2] + 0.4 k_1'[5 \text{S}_8][0.3125 \text{H}_2\text{O}]$$

In the above equations the brackets indicate concentration of the components. The analog schematic is given in Exhibit No. 1-20.

1.7.2.3 The rate constants for ( $\text{H}_2\text{S} + \text{SO}_2$ ) reaction were determined by making several computer runs and matching the experimental kinetic data with those predicted by the model. The experimental kinetic data



reported in Exhibits 1-5 through 1-8 were used for this purpose. It was found that the rate constants obtained for (H<sub>2</sub>S + SO<sub>2</sub>) reaction are approximately the same as those obtained for (H<sub>2</sub>S + SO<sub>2</sub> + H<sub>2</sub>O) reaction. It therefore follows that the rate of the reaction of (H<sub>2</sub>S + SO<sub>2</sub>) is not affected by the 20% water in the feed.

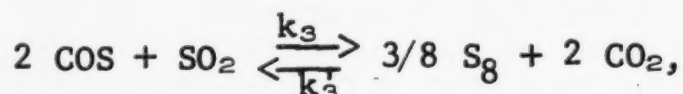
1.7.2.4 The forward rate constant for the (H<sub>2</sub>S + SO<sub>2</sub>) reaction is given in the Arrhenius plot of log k<sub>1</sub> vs 1/T°K in Exhibit No. 1-21. The rate constant is given as a function of temperature by the equation.

$$k_1 = 61.66 e^{-\frac{1305}{T}}$$

where T is in °K

COS + SO<sub>2</sub>

1.7.2.5 This reaction may be represented by



where k<sub>3</sub> is the forward rate constant and k'<sub>3</sub> is the reverse rate constant. The rate constants are referred to the SO<sub>2</sub> component. It is again assumed that S<sub>8</sub> is mainly formed in the above reaction. The scaled equations for the analog computer are:

$$-\frac{d}{dt}[8 \text{ COS}] = 0.4 k_3[8 \text{ COS}][5 \text{ SO}_2] - 0.1 k'_3[20 \text{ S}_8][8 \text{ CO}_2]$$

$$-\frac{d}{dt}[5 \text{ SO}_2] = 0.125 k_3[8 \text{ COS}][5 \text{ SO}_2] - 0.031 k'_3[20 \text{ S}_8][8 \text{ CO}_2]$$

$$-\frac{d}{dt}[20 \text{ S}_8] = -0.188 k_3[8 \text{ COS}][5 \text{ SO}_2] + 0.047 k'_3[20 \text{ S}_8][8 \text{ CO}_2]$$

$$-\frac{d}{dt}[8 \text{ CO}_2] = -0.4 k_3[8 \text{ COS}][5 \text{ SO}_2] + 0.1 k'_3[20 \text{ S}_8][8 \text{ CO}_2]$$

The analog schematic is shown in Exhibit No. 1-22. The rate constants were determined by fitting experimental data with the theoretical predictions. The experimental kinetic data reported in Exhibit No. 1-11 were used for this purpose. The Arrhenius plot of log k<sub>3</sub> vs 1/T°K is given in Exhibit No. 1-23. The rate constant may be expressed by the equation

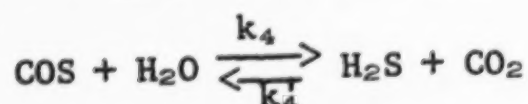


$$k_3 = 9.5 \times 10^7 e^{-\frac{11420}{T}}$$

where T is in °K

#### COS + H<sub>2</sub>O

1.7.2.6 This reaction is given by



where  $k_4$  is the forward rate constant and  $k_4'$  is the reverse rate constant. The scaled equations for the analog computer are:

$$-\frac{d}{dt}[8 \text{ COS}] = 2.5 k_4 [8 \text{ COS}][0.4 \text{ H}_2\text{O}] - 0.125 k_4' [8 \text{ H}_2\text{S}][8 \text{ CO}_2]$$

$$-\frac{d}{dt}[0.4 \text{ H}_2\text{O}] = 0.125 k_4 [8 \text{ COS}][0.4 \text{ H}_2\text{O}] - 0.00625 k_4' [8 \text{ H}_2\text{S}][8 \text{ CO}_2]$$

$$-\frac{d}{dt}[8 \text{ H}_2\text{S}] = -2.5 k_4 [8 \text{ COS}][0.4 \text{ H}_2\text{O}] + 0.125 k_4' [8 \text{ H}_2\text{S}][8 \text{ CO}_2]$$

$$-\frac{d}{dt}[8 \text{ CO}_2] = -2.5 k_4 [8 \text{ COS}][0.4 \text{ H}_2\text{O}] + 0.125 k_4' [8 \text{ H}_2\text{S}][8 \text{ CO}_2]$$

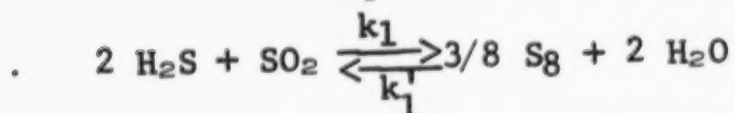
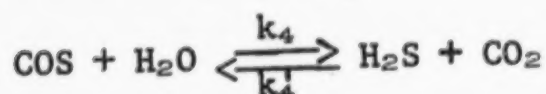
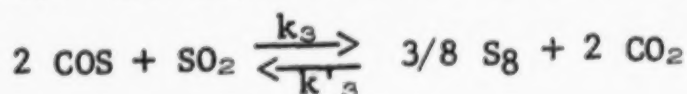
The rate constants were determined by matching the experimental kinetic data with those predicted by the model. The experimental kinetic data given in Exhibit No. 1-12 were used for this purpose. The Arrhenius plot of  $\log k_4$  vs.  $1/T^\circ\text{K}$  is given in Exhibit No. 1-25. The Arrhenius equation for the rate may be written as

$$k_4 = 16.87 e^{-\frac{2880}{T}}$$

where T is in °K

#### COS + SO<sub>2</sub> + H<sub>2</sub>O

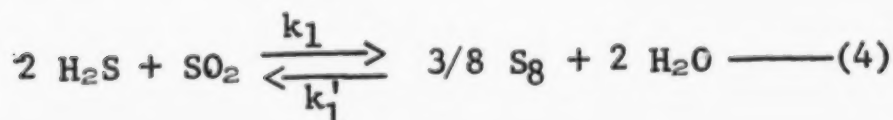
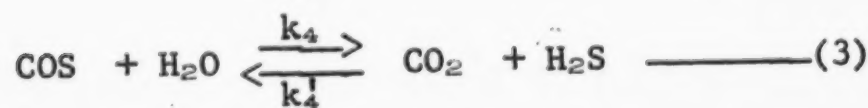
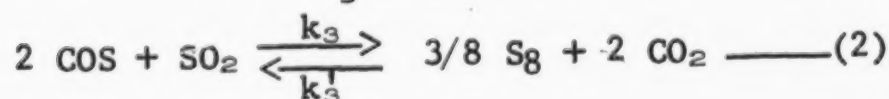
1.7.2.7 The reactions involved one given by



Using these reactions the analog schematic for (COS + SO<sub>2</sub> + H<sub>2</sub>O) was developed and is given in Exhibit No. 1-26. The rate constants for the individual reactions have already been determined. It was found that the model predicts the experimental kinetic data reported in Exhibit No. 1-13.

#### CO + SO<sub>2</sub> + H<sub>2</sub>O

1.7.2.8 The reactions taking place may be written as:



In reaction (1) above  $k_5$  is referred to the SO<sub>2</sub> component. The other rate constants have already been defined. The scaled equations considering only the forward reactions are given by

$$-\frac{d}{dt}[25 \text{ H}_2\text{S}] = 0.32 k_1 [25 \text{ H}_2\text{S}][6.25 \text{ SO}_2] - 2.5 k_4 [25 \text{ COS}][0.4 \text{ H}_2\text{O}]$$

$$-\frac{d}{dt}[6.25 \text{ SO}_2] = 0.04 k_1 [25 \text{ H}_2\text{S}][6.25 \text{ SO}_2] + 0.04 k_3 [25 \text{ COS}][6.25 \text{ SO}_2] + 0.1 k_5 [10 \text{ CO}][6.25 \text{ SO}_2]$$

$$-\frac{d}{dt}[25 \text{ COS}] = 2.5 k_4 [25 \text{ COS}][.4 \text{ H}_2\text{O}] + 0.32 k_3 [25 \text{ COS}][6.25 \text{ SO}_2] - 0.4 k_5 [10 \text{ CO}][6.25 \text{ SO}_2]$$

$$-\frac{d}{dt}[.4 \text{ H}_2\text{O}] = 0.04 k_4 [25 \text{ COS}][.4 \text{ H}_2\text{O}] - .005 k_1 [25 \text{ H}_2\text{S}][6.25 \text{ SO}_2]$$

$$-\frac{d}{dt}[10 \text{ CO}] = 0.48 k_5 [10 \text{ CO}][6.25 \text{ SO}_2]$$

$$-\frac{d}{dt}[10 \text{ CO}_2] = -k_4 [25 \text{ COS}][.4 \text{ H}_2\text{O}] - 0.128 k_3 [25 \text{ COS}][6.25 \text{ SO}_2] + 0.32 k_5 [10 \text{ CO}][6.25 \text{ SO}_2]$$

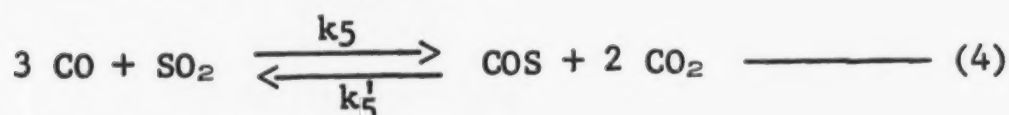
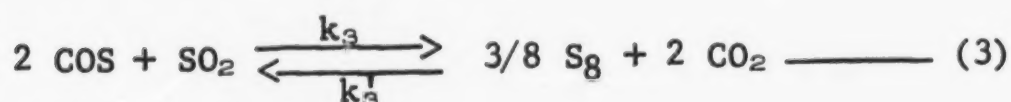
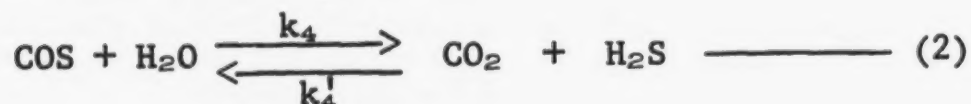
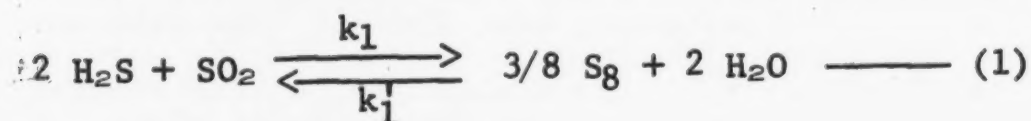
The analog schematic is given in Exhibit No. 1-27. By knowing rate constants  $k_1$ ,  $k_3$  and  $k_4$ , the rate constant  $k_5$  was determined by matching the theoretical predictions with the experimental data. The experimental data given in Exhibit No. 1-14 were used for this purpose. The Arrhenius plot of  $\log k_5 V_s 1/T$  is given in Exhibit 1-28. The rate constant equation may then be written

$$k_5 = 3.63 \times 10^5 e^{-\frac{8250}{T}}$$

where  $T$  is in  $^{\circ}\text{K}$

### 1.7.3 The Total System

1.7.3.1 The overall kinetic model was developed on the basis of the following reactions.



The rate equations may be written as:

$$\begin{aligned} \frac{d}{dt} (\text{H}_2\text{S}) = & -2 k_1 (\text{H}_2\text{S})(\text{SO}_2) + 2 \frac{k_1}{K_{S_1}} (\text{S}_8)(\text{H}_2\text{O}) + k_4 (\text{COS})(\text{H}_2\text{O}) \\ & - \frac{k_4}{K_{S_4}} (\text{CO}_2)(\text{H}_2\text{S}) \end{aligned}$$

$$\begin{aligned} \frac{d}{dt} (\text{SO}_2) = & -k_5 (\text{CO})(\text{SO}_2) + \frac{k_5}{K_{S_5}} (\text{COS})(\text{CO}_2) - k_3 (\text{COS})(\text{SO}_2) \\ & + \frac{k_3}{K_{S_3}} (\text{S}_8)(\text{CO}_2) - k_1 (\text{H}_2\text{S})(\text{SO}_2) + \frac{k_1}{K_{S_1}} (\text{S}_8)(\text{H}_2\text{O}) \end{aligned}$$

$$\begin{aligned} \frac{d}{dt} (\text{COS}) = & -k_4 (\text{COS})(\text{H}_2\text{O}) + \frac{k_4}{K_{S_4}} (\text{CO}_2)(\text{H}_2\text{S}) - 2 k_3 (\text{COS})(\text{SO}_2) \\ & + \frac{2k_3}{K_{S_3}} (\text{S}_8)(\text{CO}_2) + k_5 (\text{CO})(\text{SO}_2) - \frac{k_5}{K_{S_5}} (\text{COS})(\text{CO}_2) \end{aligned}$$



$$\frac{d}{dt}(\text{CO}) = -3 k_5(\text{CO})(\text{SO}_2) + 3 \frac{k_5}{K_{S_5}}(\text{COS})(\text{CO}_2)$$

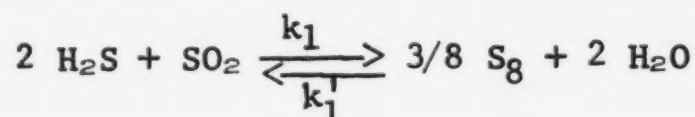
$$(\text{H}_2\text{O}) = (\text{H}_2\text{O})_{\text{IC}} + (\text{H}_2\text{S})_{\text{IC}} - (\text{H}_2\text{S})$$

$$(\text{S}_8) = ((\text{SO}_2)_{\text{IC}} + (\text{H}_2\text{S})_{\text{IC}} + (\text{COS})_{\text{IC}} - (\text{SO}_2) - (\text{H}_2\text{S}) - (\text{COS}))/8 + (\text{S}_8)_{\text{IC}}$$

$$(\text{CO}_2) = (\text{CO}_2)_{\text{IC}} + (\text{CO})_{\text{IC}} + (\text{COS})_{\text{IC}} - (\text{CO}) - (\text{COS})$$

In above equation  $K_{S_1}$ ,  $K_{S_4}$ ,  $K_{S_3}$ ,  $K_{S_5}$  are the Pseudo-Equilibrium constants of reaction (1), (2), (3), and (4) respectively. It may be noted that concentrations of water, sulfur and carbon dioxide were calculated by material balance.

1.7.3.2 The forward rate constants for the above reactions have already been determined using analog programs. The reverse rate constants were determined in such a manner that the system reaches the theoretical equilibrium conditions at infinite contact time. The reverse rate constants were calculated from what may be called the Pseudo-Equilibrium constant and the method may be illustrated from the following example



$$\frac{d}{dt}(\text{SO}_2) = -k_1(\text{H}_2\text{S})(\text{SO}_2) + k'_1(\text{S}_8)(\text{H}_2\text{O})$$

$$\text{At Equilibrium } \frac{d}{dt}(\text{SO}_2) = 0$$

$$\therefore k_1(\text{H}_2\text{S})(\text{SO}_2) = k'_1(\text{S}_8)(\text{H}_2\text{O})$$

$$\therefore \frac{k_1}{k'_1} = \frac{(\text{S}_8)(\text{H}_2\text{O})}{(\text{H}_2\text{S})(\text{SO}_2)}$$

Define  $K_{S_1} = k_1/k'_1$ , where  $K_{S_1}$  is called the Pseudo-Equilibrium constant. The actual equilibrium constant is related to Pseudo-Equilibrium constant by

$$K_{\text{eq}} = K_{S_1} \frac{(\text{H}_2\text{O})_{\text{eq}}(\text{S}_8)_{\text{eq}}^{-5/8}}{(\text{H}_2\text{S})_{\text{eq}}}$$

$$K_{S1} = \frac{(H_2S)_{eq} (S_8)_{eq}^{5/8}}{(H_2O)_{eq}} K_{eq}$$

By knowing the actual equilibrium constant and the equilibrium compositions, the Pseudo-Equilibrium constant may be calculated. Once the Pseudo-Equilibrium constant is known, the reverse rate constant may be calculated.

1.7.3.3 The overall kinetic model is a digital program written in Fortran IV. It consists of subroutines such as the Complex Equilibrium program (12) and the fourth order Runge-Kutta numerical integration technique(13). For a given feed composition and temperature, the program calculates the equilibrium composition of the various constituents and hence the Pseudo-Equilibrium constant. From the known values of Pseudo-Equilibrium constant and the forward rate constants, the reverse rate constants are calculated. The forward rate constants and the reverse rate constants of all the four reactions are now known. The program then integrates the differential rate equations listed above using the fourth order Runge-Kutta numerical integration. Then the compositions of the various constituents are printed out as a function of the contact time. A listing of the main digital program is given in Exhibit No. 1-30. This work was done on an IBM 1130 computer.

1.7.3.4 The user must specify the following information.

- (1) System feed composition, mol.%
- (2) Feed temperature in °F
- (3) Print time and integration interval in seconds.

The calculated results include

- (1) Reverse rate constants
- (2) Equilibrium composition, mol.%
- (3) Percent composition of the various constituents as a function of contact time.

1.7.3.5 The experimental kinetic data of the overall Claus reaction have already been reported in Exhibit No. 1-16. These may now be compared with those predicted by the model. As a first hand trial the forward rate constants obtained from the analog computations were used in the model. In general, the agreements between the predicted results and the experimental results were good except for constituents such as COS, CO and CO<sub>2</sub>. Therefore the rate constants  $k_3$ ,  $k_4$  and  $k_5$  were adjusted to get better agreement between calculated

and experimental results. The search for these rate constants was essentially a trial and error process. Several computer runs had to be made at various temperatures and feed compositions, before arriving at the best values. It was found that the agreement between calculated and experimental results is good with the following equations for the rate constants.

$$k_1 = 61.66e^{-\frac{1305}{T}}$$

$$k_4 = 2.75e^{-\frac{2080}{T}}$$

$$k_3 = 2.09 \times 10^7 e^{-\frac{10870}{T}}$$

$$k_5 = 813e^{-\frac{6580}{T}}$$

In the above equations T is in °K. The calculated results are compared with the experimental values in Exhibit No. 1-29. The computer printouts are presented as Exhibit No. 1-31. It may be seen that the agreement between calculated and experimental results is very good in the normal Claus range. However at higher temperatures of 700°F, the agreement is not good. The conversion predicted by the model is less than those of the experimental values. In fact, the experimental results show that the equilibrium is violated. The conversions obtained by the experiment are even better than what equilibrium permits, which of course is not possible. More than equilibrium conversions are explained on the basis that further reaction must be taking place at lower temperatures (where equilibrium is more favorable) in the bottom leg and sample tube after the reaction products leave the catalyst bed at 700°F.

1.7.3.6 From the design point of view the model is reliable even at 700°F. The model is more conservative than the experimental values. Equilibrium limitations have been incorporated in the model. For the sake of simplicity only the S<sub>8</sub> form of sulfur species is taken into account in the model. This is a reasonable assumption in the normal Claus range. However other forms of sulfur such as S<sub>6</sub>, S<sub>2</sub> and S<sub>4</sub> also are present at 700°F. Therefore the model could be improved by taking into consideration the other forms of sulfur species.

1.7.3.7 The overall model is quite flexible. It reduces to the individual reaction models under individual reaction conditions. Thus we can even study the kinetics of the individual reactions from the overall model.

1.7.3.8 In the temperature range of 400 to 700°F, hydrogen does not react with any constituent and it passes through the Claus process as an inert. Therefore hydrogen was included in the inerts and no provision was made for printing out of hydrogen composition as a function of time.

## 1.8 BIBLIOGRAPHY

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EXHIBIT NO. 1-1  
EXPERIMENTAL KINETIC DATA  
CATALYST - POROCAL LPD  
SYSTEM - (H<sub>2</sub>S + SO<sub>2</sub> + H<sub>2</sub>O)  
FEED - 20% WATER

| Contact Time<br>Seconds | Bed Ht.<br>Inches | Linear Velocity<br>ft/sec. | Run No. | Nominal Temp.<br>°F | Gas Composition - Volume % |                 |                  |                 | % Conv. of<br>H <sub>2</sub> S<br>H <sub>2</sub> /SO <sub>2</sub> =2:1 | % Conv. of<br>SO <sub>2</sub><br>H <sub>2</sub> S/SO <sub>2</sub> =2:1 |
|-------------------------|-------------------|----------------------------|---------|---------------------|----------------------------|-----------------|------------------|-----------------|------------------------------------------------------------------------|------------------------------------------------------------------------|
|                         |                   |                            |         |                     | Feed (Dry Basis)           |                 | Products         |                 |                                                                        |                                                                        |
|                         |                   |                            |         |                     | H <sub>2</sub> S           | SO <sub>2</sub> | H <sub>2</sub> S | SO <sub>2</sub> |                                                                        |                                                                        |
|                         |                   |                            |         |                     |                            |                 |                  |                 |                                                                        |                                                                        |
| 1                       | 10"               | 0.42                       | J-16R   | 500                 | 2.86                       | 1.49            | 0.39             | 0.22            | 86                                                                     | 86                                                                     |
| 1                       | 20"               | 0.84                       | J-20R   | 500                 | 3.0                        | 1.50            | 0.56             | 0.25            | 82                                                                     | 83                                                                     |

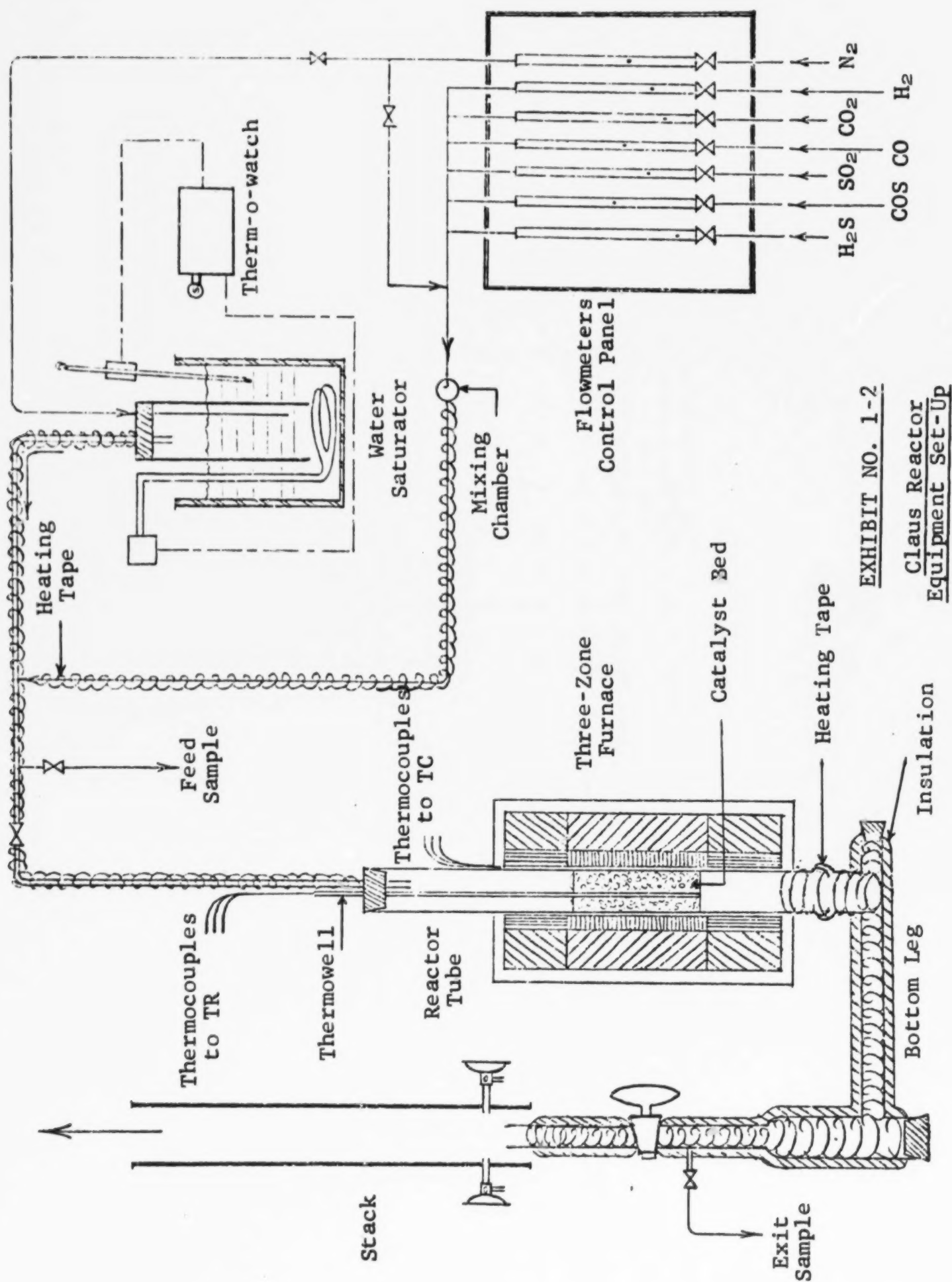


EXHIBIT NO. 1-2

Claus Reactor  
Equipment Set-Up

Exhibit No. 1-3

System - (COS + SO<sub>2</sub> + H<sub>2</sub>O)  
 Porocel LPD Catalyst  
 Typical Temperature Profile, °C

| Contact Time Sec. | Bed Ht. from Bottom of Bed In Inches | Nominal Temperature |               |               |               |
|-------------------|--------------------------------------|---------------------|---------------|---------------|---------------|
|                   |                                      | 400°F (204°C)       | 475°F (246°C) | 550°F (288°C) | 700°F (371°C) |
| 1/2               | 3/4                                  | 210                 | 245           | 288           | 370           |
|                   | 3 3/4                                | 211                 | 245           | 288           | 368           |
|                   | 6 3/4                                | 211                 | 248           | 292           | 375           |
|                   | 10(Top)                              | 212                 | 250           | 285           | 370           |
| 1                 | 3/4                                  | 209                 | 254           | 290           | 370           |
|                   | 3 3/4                                | 210                 | 253           | 289           | 376           |
|                   | 6 3/4                                | 210                 | 255           | 289           | 383           |
|                   | 10(Top)                              | 205                 | 253           | 285           | 370           |
| 2<br>or<br>2.5    | 3/4                                  | 202                 | 250           | 286           | 368           |
|                   | 3 3/4                                | 206                 | 248           | 288           | 368           |
|                   | 6 3/4                                | 206                 | 255           | 292           | 374           |
|                   | 10(Top)                              | 208                 | 255           | 290           | 370           |



EXHIBIT NO. 1-4

System - H<sub>2</sub>S + SO<sub>2</sub>  
 Porocel LPD Catalyst  
Typical Bed Temperature Profiles, °C

| Contact Time Sec. | Bed Ht. from Bottom of Bed in Inches | Nominal Temperature      |                          |                          |                          |
|-------------------|--------------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
|                   |                                      | 450°F(232°C)             | 500°F(260°C)             | 550°F(288°C)             | 700°F(371°C)             |
| 1/16              | 1/4<br>3 (Top)                       |                          |                          | 287<br>285               | 368<br>373               |
| 1/8               | 1/4<br>3 1/4<br>6 (Top)              |                          |                          | 308<br>300<br>280        | 378<br>375<br>363        |
| 1/8               | 1/4<br>3 (Top)                       | 236<br>234               | 263<br>259               |                          |                          |
| 1/4               | 1/4<br>3 1/4<br>6 1/4<br>10 (Top)    | 230<br>232<br>234<br>228 | 260<br>264<br>260<br>255 | 291<br>303<br>317<br>282 | 370<br>375<br>395<br>387 |

EXHIBIT NO. 1-5  
EXPERIMENTAL KINETIC DATA  
CATALYST - POROCCEL LPD  
SYSTEM - H<sub>2</sub>S + SO<sub>2</sub>

| Contact Time<br>sec. | Run No. | Nominal<br>Temp.<br>°F | Gas Composition - Volume % |                 |                                 |                 |
|----------------------|---------|------------------------|----------------------------|-----------------|---------------------------------|-----------------|
|                      |         |                        | Feed                       |                 | Products (Dry and S-Free Basis) |                 |
|                      |         |                        | H <sub>2</sub> S           | SO <sub>2</sub> | H <sub>2</sub> S                | SO <sub>2</sub> |
| 1/2                  | 7       | 400                    | 11.65                      | 1.8             | 9.6                             | 1.13            |
| 1                    | 8       | 400                    | 12.5                       | 2.05            | 10.83                           | 1.22            |
| 2                    | 9       | 400                    | 11.9                       | 1.88            | 8.93                            | 0.56            |
| 1/2                  | 2       | 550                    | 1.4                        | 10.9            | trace                           | 10.4            |
| 1                    | 1       | 550                    | 1.94                       | 10.15           | trace                           | 9.26            |
| 2                    | 3       | 550                    | 1.89                       | 11.00           | trace                           | 9.93            |
| 1/2                  | 6       | 700                    | 5.93                       | 3.15            | 0.72                            | 0.64            |
| 1                    | 4       | 700                    | 6.38                       | 3.05            | 0.73                            | 0.5             |
| 2                    | 5       | 700                    | 6.22                       | 3.09            | 0.69                            | 0.67            |

EXHIBIT NO. 1-6  
Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - H<sub>2</sub>S + SO<sub>2</sub>

| Contact Time Sec. | Run No. | Bed Ht. in Inches | Nominal Temp. °F | Gas Composition - Volume % |                 |                                 |                 |
|-------------------|---------|-------------------|------------------|----------------------------|-----------------|---------------------------------|-----------------|
|                   |         |                   |                  | Feed                       |                 | Products (Dry and S-free Basis) |                 |
|                   |         |                   |                  | H <sub>2</sub> S           | SO <sub>2</sub> | H <sub>2</sub> S                | SO <sub>2</sub> |
| 1/8               | F-4     | 3                 | 450              | 6.04                       | 3.06            | 3.16                            | 1.68            |
| 1/4               | *E-1    | 10                | 450              | 5.77                       | 2.86            | 3.64                            | 1.95            |
| 1/8               | F-3     | 3                 | 500              | 5.33                       | 2.74            | 0.78                            | 0.63            |
| 1/4               | *D-2    | 10                | 500              | 6.05                       | 2.92            | 2.07                            | 1.13            |
| 1/2               | D-1     | 10                | 500              | 5.85                       | 3.0             | .67                             | 0.68            |
| 1/16              | F-1     | 3                 | 550              | 5.76                       | 2.77            | 1.86                            | 0.84            |
| 1/8               | 2AA     | 6                 | 550              | 5.6                        | 2.65            | 0.84                            | 0.36            |
| 1/4               | 2B      | 10                | 550              | 6.36                       | 3.23            | 0.34                            | 0.33            |
| 1/16              | F-2     | 3                 | 700              | 4.84                       | 2.6             | 1.17                            | 0.85            |
| 1/9               | 2A      | 6                 | 700              | 5.99                       | 2.9             | 0.91                            | 0.34            |
| 1/4               | 6B      | 10                | 700              | 6.59                       | 3.3             | 0.89                            | 0.44            |

\* It was found after Runs E-1 and D-2 that liquid sulfur had deposited on the catalyst which probably could have poisoned the catalyst.

EXHIBIT NO. 1-7

Experimental Kinetic Data

Catalyst - Porocel LPD

System - (H<sub>2</sub>S + SO<sub>2</sub>)

| Contact<br>Time,<br>sec. | Run<br>No. | Nominal<br>Temp.,<br>°F | Gas Composition - Volume % |                 |                                    |                 |
|--------------------------|------------|-------------------------|----------------------------|-----------------|------------------------------------|-----------------|
|                          |            |                         | Feed                       |                 | Products<br>(Dry and S-Free Basis) |                 |
|                          |            |                         | H <sub>2</sub> S           | SO <sub>2</sub> | H <sub>2</sub> S                   | SO <sub>2</sub> |
| 1/2                      | P-1        | 400                     | 2.94                       | 1.55            | 0.33                               | 0.26            |
| 1                        | P-2        | 400                     | 2.69                       | 1.40            | 0.0                                | 0.11            |
| 1/2                      | P-3        | 450                     | 2.97                       | 1.47            | 0.075                              | 0.0125          |
| 1                        | P-4        | 450                     | 2.94                       | 1.39            | 0.06                               | 0.00            |



EXHIBIT NO. 1-8

Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - ( $H_2S + SO_2 + H_2O$ )

| Contact Time Sec. | Run No. | Nominal Temp. °F | Gas Composition - Volume % |        |                                 |        |
|-------------------|---------|------------------|----------------------------|--------|---------------------------------|--------|
|                   |         |                  | Feed (Dry Basis)           |        | Products (Dry and S-free Basis) |        |
|                   |         |                  | $H_2S$                     | $SO_2$ | $H_2S$                          | $SO_2$ |
| 1                 | J-4     | 400              | 2.45                       | 1.17   | 0.16                            | 0.06   |
| 2.5               | J-5     | 400              | 2.2                        | 1.0    | 0.45                            | 0.025  |
| 1/2               | J-7     | 450              | 2.62                       | 1.08   | 0.51                            | 0.03   |
| 2.5               | J-6     | 450              | 2.08                       | 0.83   | 0.7                             | 0.04   |
| 1/2               | J-1     | 500              | 6.77                       | 3.73   | 0.52                            | 0.60   |
| 2.0               | J-8     | 500              | 2.74                       | 1.13   | 1.05                            | 0.23   |
| 1/16              | *J-9    | 550              | 2.88                       | 1.55   | 0.96                            | 0.66   |
| 1/16              | *J-10   | 700              | 3.19                       | 1.61   | 1.28                            | 0.56   |

\* Runs J-9 and J-10 are made with 3" of bed.

Exhibit No. 1-9  
Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - (H<sub>2</sub> + SO<sub>2</sub> + H<sub>2</sub>O)  
Feed - 20% Water

| Contact Time, Sec. | Run No. | Nominal Temp. °F | Gas Composition - Volume % |                 |                                 |                 |                  |
|--------------------|---------|------------------|----------------------------|-----------------|---------------------------------|-----------------|------------------|
|                    |         |                  | Feed (Dry Basis)           |                 | Products (Dry and S-Free Basis) |                 |                  |
|                    |         |                  | H <sub>2</sub>             | SO <sub>2</sub> | H <sub>2</sub>                  | SO <sub>2</sub> | H <sub>2</sub> S |
| 2.5                | M-1     | 400              | 1.31                       | 1.27            | 1.28                            | 1.22            | 0.0              |
| 2.0                | M-2     | 550              | 1.19                       | 1.23            | 1.18                            | 1.18            | 0.0              |
| 1/2                | M-3     | 700              | 0.83                       | 1.38            | 0.83                            | 1.38            | 0.0              |
| 1                  | M-4     | 700              | 1.27                       | 1.44            | 1.02                            | 1.34            | 0.0              |
| 2.0                | M-5     | 700              | 1.30                       | 1.08            | 1.25                            | 1.08            | 0.09             |

EXHIBIT NO. 1-10

Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - (COS + N<sub>2</sub>)

| Contact<br>Time<br>Sec. | Run No. | Nominal<br>Temp.<br>°F | Gas Composition - Volume % |                                 |                 |                 |       |
|-------------------------|---------|------------------------|----------------------------|---------------------------------|-----------------|-----------------|-------|
|                         |         |                        | Feed<br>COS                | Products (Dry and S-free Basis) |                 |                 |       |
|                         |         |                        |                            | COS                             | CO <sub>2</sub> | CS <sub>2</sub> | CO    |
| 1                       | H-4     | 400                    | 2.04                       | 1.81                            | 0.1             | 0.24            | Trace |
| 2                       | H-3     | 400                    | 1.82                       | 1.39                            | 0.14            | 0.38            | 0.01  |
| 0.554                   | 22R     | 550                    | 2.26                       | 1.78                            | 0.38            | 0.26            | 0.01  |
| 2.22                    | H-2     | 550                    | 2.05                       | 1.33                            | 0.25            | 0.59            | 0.01  |
| 1/2                     | H-5     | 700                    | 1.92                       | 1.22                            | 0.31            | 0.50            | 0.02  |
| 1                       | H-6     | 700                    | 1.81                       | 1.11                            | 0.31            | 0.45            | 0.03  |

EXHIBIT NO. 1-11

Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - (COS + SO<sub>2</sub>)

| Contact Time Sec. | Run No. | Nominal Temp. °F | Gas Composition - Volume % |                 |                                 |                 |                 |
|-------------------|---------|------------------|----------------------------|-----------------|---------------------------------|-----------------|-----------------|
|                   |         |                  | Feed (Dry-Basis)           |                 | Products (Dry and S-Free Basis) |                 |                 |
|                   |         |                  | COS                        | SO <sub>2</sub> | COS                             | SO <sub>2</sub> | CO <sub>2</sub> |
| 1                 | S-5     | 400              | 0.79                       | 1.39            | 0.78                            | 1.39            | < .01           |
| 2.0               | S-6     | 400              | 0.61                       | 1.38            | 0.60                            | 1.39            | < .01           |
| 1                 | S-1R    | 550              | 0.71                       | 1.49            | 0.45                            | 1.35            | 0.18            |
| 2                 | S-2R    | 550              | 0.47                       | 1.41            | 0.21                            | 1.29            | 0.21            |
| 1/2               | S-3     | 700              | 0.87                       | 1.61            | 0.02                            | 1.14            | 0.62            |
| 1                 | S-4     | 700              | 0.69                       | 1.47            | 0.0                             | 1.1             | 0.51            |



Exhibit No. 1-12

Experimental Kinetic Data

Catalyst - Porocel LPD

System - (COS + H<sub>2</sub>O)

Feed - 20% Water

| Contact<br>Time<br>Sec. | Run No. | Nominal<br>Temp.<br>°F | Gas Composition - Volume % |  |                                 |                  |
|-------------------------|---------|------------------------|----------------------------|--|---------------------------------|------------------|
|                         |         |                        | Feed (Dry-Basis)           |  | Products (Dry and S-Free Basis) |                  |
|                         |         |                        | COS                        |  | COS                             | H <sub>2</sub> S |
| 1/2                     | N6      | 400                    | 0.9                        |  | 0.37                            | 0.46             |
| 1                       | N7      | 400                    | 0.94                       |  | 0.12                            | 0.61             |
| 2.5                     | N1      | 400                    | 0.94                       |  | 0.02                            | 0.59             |
| 1/2                     | N8      | 550                    | 0.87                       |  | 0.27                            | 0.53             |
| 1                       | N9      | 550                    | 0.86                       |  | 0.12                            | 0.62             |
| 2                       | N2      | 550                    | 0.88                       |  | 0.01                            | 0.89             |
| 1/2                     | N3      | 700                    | 0.89                       |  | 0.04                            | 0.83             |
| 1                       | N4      | 700                    | 0.89                       |  | 0.04                            | 0.67             |
| 2                       | N5      | 700                    | 1.04                       |  | 0.0                             | 0.9              |

Exhibit No. 1-13

Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - (COS + SO<sub>2</sub> + H<sub>2</sub>O)  
Feed - 20% Water

| Contact Time Sec. | Run No. | Nominal Temp. °F | Gas Composition - Volume % |                 |                                 |                 |                 |                  |
|-------------------|---------|------------------|----------------------------|-----------------|---------------------------------|-----------------|-----------------|------------------|
|                   |         |                  | Feed (Dry-Basis)           |                 | Products (Dry and S-Free Basis) |                 |                 |                  |
|                   |         |                  | COS                        | SO <sub>2</sub> | COS                             | SO <sub>2</sub> | CO <sub>2</sub> | H <sub>2</sub> S |
| 1/2               | K- 7    | 400              | 0.9                        | 1.49            | 0.59                            | 1.29            | 0.19            | 0.02             |
| 1                 | K- 8    | 400              | 0.945                      | 1.67            | 0.33                            | 1.21            | 0.43            | 0.035            |
| 2.5               | K- 2    | 400              | 0.79                       | 1.19            | 0.01                            | 0.2             | 0.79            | 0.13             |
| 1/2               | K-13    | 475              | 0.89                       | 1.50            | 0.50                            | 1.38            | 0.29            | 0.11             |
| 1                 | K-12    | 475              | 0.88                       | 1.55            | 0.2                             | 1.45            | 0.54            | 0.22             |
| 2.5               | K-11    | 475              | 1.09                       | 1.18            | 0.06                            | 0.79            | 0.78            | 0.17             |
| 1/2               | K- 9    | 550              | 0.83                       | 1.48            | 0.35                            | 1.30            | 0.47            | 0.04             |
| 1                 | K-10    | 550              | 0.85                       | 1.38            | 0.1                             | 1.1             | 0.61            | 0.18             |
| 2                 | K- 3    | 550              | 0.97                       | 1.20            | 0.0                             | 0.9             | 0.8             | 0.28             |
| 1/2               | K- 4    | 700              | 0.89                       | 1.47            | 0.035                           | 1.25            | 0.76            | 0.64             |
| 1                 | K- 5    | 700              | 0.91                       | 1.45            | 0.02                            | 1.37            | 0.79            | 0.64             |
| 2                 | K- 6    | 700              | 0.98                       | 1.12            | 0.0                             | 0.94            | 0.85            | 0.68             |

Exhibit No.1-14

Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - (CO + SO<sub>2</sub> + H<sub>2</sub>O)  
Feed - 20% Water

| Contact Time, Sec. | Run No. | Nominal Temp. °F | Gas Composition - Volume % |                 |                                 |                 |                 |       |                  |
|--------------------|---------|------------------|----------------------------|-----------------|---------------------------------|-----------------|-----------------|-------|------------------|
|                    |         |                  | Feed (Dry Basis)           |                 | Products (Dry and S-Free Basis) |                 |                 |       |                  |
|                    |         |                  | CO                         | SO <sub>2</sub> | CO                              | SO <sub>2</sub> | CO <sub>2</sub> | COS   | H <sub>2</sub> S |
| 1                  | L-6     | 400              | 0.79                       | 1.56            | 0.73                            | 1.52            | 0.0             | 0.0   | 0.0              |
| 2.5                | L-1     | 400              | 0.93                       | 1.27            | 0.76                            | 1.44            | 0.0             | 0.0   | 0.0              |
| 1.0                | L-7     | 550              | 0.72                       | 1.51            | 0.71                            | 1.51            | 0.0             | 0.0   | 0.0              |
| 2.0                | L-2     | 550              | 0.83                       | 1.30            | 0.76                            | 1.28            | 0.06            | 0.01  | 0.0              |
| 1.0                | L-9     | 600              | 0.69                       | 1.51            | 0.46                            | 1.44            | 0.13            | 0.01  | 0.01             |
| 2.0                | L-8     | 600              | 0.71                       | 1.43            | 0.39                            | 1.25            | 0.27            | 0.016 | 0.04             |
| 1/2                | L-3     | 700              | 0.8                        | 1.4             | 0.68                            | 1.38            | 0.08            | 0.01  | 0.01             |
| 1                  | L-4     | 700              | 0.76                       | 1.38            | 0.56                            | 1.3             | 0.15            | 0.01  | 0.02             |
| 2                  | L-5     | 700              | 0.85                       | 1.08            | 0.46                            | 0.9             | 0.34            | 0.0   | 0.06             |

Exhibit No. 1-15

Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - CO + H<sub>2</sub>O  
Feed - 20% Water

| Contact Time<br>Sec. | Run No. | Nominal<br>Temp.<br>°F | Gas Composition - Volume % |                                 |
|----------------------|---------|------------------------|----------------------------|---------------------------------|
|                      |         |                        | Feed (Dry-Basis)           | Products (Dry and S-Free Basis) |
|                      |         |                        | CO                         | CO                              |
| 2.0                  | Q-2     | 550                    | 0.80                       | 0.79                            |
| 1.0                  | Q-3     | 700                    | 0.66                       | 0.68                            |
| 2.0                  | Q-4     | 700                    | 0.76                       | 0.75                            |



EXHIBIT NO. 1-16  
EXPERIMENTAL KINETIC DATA  
CATALYST - POROCEL LPD  
SYSTEM - OVERALL REACTION  
FEED - 20% WATER

| Contact<br>Time<br>Sec. | Run<br>No. | Nominal<br>Temp.<br>°F. | Gas Composition - Volume % |      |                |                  |                 |                 |                                 |      |                |                  |                 |                 |
|-------------------------|------------|-------------------------|----------------------------|------|----------------|------------------|-----------------|-----------------|---------------------------------|------|----------------|------------------|-----------------|-----------------|
|                         |            |                         | Feed (Dry - Basis)         |      |                |                  |                 |                 | Products (Dry and S-free Basis) |      |                |                  |                 |                 |
|                         |            |                         | CO                         | COS  | H <sub>2</sub> | H <sub>2</sub> S | SO <sub>2</sub> | CO <sub>2</sub> | CO                              | COS  | H <sub>2</sub> | H <sub>2</sub> S | SO <sub>2</sub> | CO <sub>2</sub> |
| 1/4                     | V-12       | 400                     | 0.98                       | 0.98 | 0.8            | 1.56             | 3.10            | 6.7             | 0.98                            | 0.72 | 0.8            | 0.26             | 2.06            | 6.96            |
| 1/2                     | V-7        | 400                     | 0.98                       | 0.97 | 0.8            | 1.38             | 3.31            | 5.23            | 0.98                            | 0.63 | 0.8            | 0.04             | 2.55            | 5.37            |
| 1                       | V-8        | 400                     | 0.84                       | 1.01 | 0.8            | 1.57             | 2.42            | 6.85            | 0.84                            | 0.62 | 0.8            | 0.0              | 1.33            | 7.17            |
| 2                       | V-9        | 400                     | 0.83                       | 0.82 | 0.8            | 1.61             | 2.42            | 6.5             | 0.83                            | 0.13 | 0.8            | 0.03             | 1.08            | 6.84            |
| 1/8                     | V-11       | 550                     | 0.88                       | 0.95 | 0.8            | 3.33             | 3.60            | 6.2             | 0.88                            | 0.71 | 0.8            | 1.35             | 2.9             | 6.4             |
| 1/2                     | V-1        | 550                     | 0.95                       | 0.99 | 0.8            | 3.67             | 3.60            | 6.46            | 0.95                            | 0.39 | 0.8            | 0.31             | 1.42            | 6.99            |
| 1                       | V-2        | 550                     | 0.78                       | 0.95 | 0.8            | 3.19             | 2.99            | 7.07            | 0.78                            | 0.23 | 0.8            | 0.40             | 1.19            | 7.66            |
| 2                       | V-3        | 550                     | 0.86                       | 0.85 | 0.8            | 3.48             | 3.16            | 5.7             | 0.81                            | 0.0  | 0.8            | 0.3              | 0.97            | 6.48            |
| 1/8                     | V-10       | 700                     | 0.92                       | 1.03 | 0.8            | 3.92             | 3.91            | 6.39            | 0.85                            | 0.36 | 0.8            | 1.59             | 2.16            | 6.77            |
| 1/2                     | V-4        | 700                     | 0.98                       | 1.07 | 0.8            | 3.17             | 3.23            | 6.12            | 0.85                            | 0.08 | 0.8            | 1.05             | 1.96            | 6.89            |
| 1                       | V-5        | 700                     | 0.78                       | 0.90 | 0.8            | 3.17             | 3.01            | 6.92            | 0.68                            | 0.04 | 0.8            | 1.28             | 1.48            | 7.71            |
| 2                       | V-6        | 700                     | 0.85                       | 0.82 | 0.8            | 3.38             | 3.48            | 5.63            | 0.54                            | 0.0  | 0.8            | 1.47             | 1.33            | 6.91            |

EXHIBIT NO. 1-17

Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - H<sub>2</sub>S + SO<sub>2</sub> + CO

| Contact Time Sec. | Run No. | Nominal Temp. °F | Gas Composition - Volume % |                 |      |                 |     |                 |                               |                 |      |                 |     |                 |  |
|-------------------|---------|------------------|----------------------------|-----------------|------|-----------------|-----|-----------------|-------------------------------|-----------------|------|-----------------|-----|-----------------|--|
|                   |         |                  | Feed                       |                 |      |                 |     |                 | Products (Dry 4 S-Free Basis) |                 |      |                 |     |                 |  |
|                   |         |                  | H <sub>2</sub> S           | SO <sub>2</sub> | CO   | CO <sub>2</sub> | COS | CS <sub>2</sub> | H <sub>2</sub> S              | SO <sub>2</sub> | CO   | CO <sub>2</sub> | COS | CS <sub>2</sub> |  |
|                   |         |                  |                            |                 |      |                 |     |                 |                               |                 |      |                 |     |                 |  |
| 1                 | C-1     | 500°F            | 3.14                       | 5.41            | 6.45 | .05             | .01 | ND              | ND                            | 4.66            | 7.34 | .07             | .02 | ND              |  |
| 2                 | C-2     | 500°F            | 3.25                       | 4.88            | 5.53 | .04             | .01 | ND              | ND                            | 3.41            | 5.84 | .07             | .02 | ND              |  |

ND - None Detected

EXHIBIT NO. 1-18

Experimental Kinetic Data  
Catalyst - Porocel LPD  
System - (H<sub>2</sub>S + SO<sub>2</sub> + H<sub>2</sub>O + CO<sub>2</sub>)  
Feed - 20% Water

| Contact Time<br>Sec. | Run No. | Nominal Temp.<br>°F | Gas Composition - Volume % |                 |                 |                                 |                 |                 | Conv.<br>of<br>$\frac{\text{H}_2\text{S}}{\text{SO}_2}$ for<br>$\frac{\text{H}_2\text{S}}{\text{SO}_2} = 2:1$ | Conv.<br>of<br>$\frac{\text{SO}_2}{\text{H}_2\text{S}} = 2:1$ |
|----------------------|---------|---------------------|----------------------------|-----------------|-----------------|---------------------------------|-----------------|-----------------|---------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
|                      |         |                     | Feed (Dry-Basis)           |                 |                 | Products (Dry and S-free Basis) |                 |                 |                                                                                                               |                                                               |
|                      |         |                     | H <sub>2</sub> S           | SO <sub>2</sub> | CO <sub>2</sub> | H <sub>2</sub> S                | SO <sub>2</sub> | CO <sub>2</sub> |                                                                                                               |                                                               |
| 1                    | J-16    | 500                 | 2.76                       | 1.38            | 0               | 0.34                            | 0.13            | 0               | 88                                                                                                            | 91                                                            |
| 1                    | J-17    | 500                 | 2.97                       | 1.41            | 5.14            | 0.68                            | 0.19            | 5.14            | 81                                                                                                            | 87                                                            |
| 1                    | J-18    | 500                 | 2.89                       | 1.37            | 10.39           | 0.38                            | 0.15            | 10.39           | 92                                                                                                            | 89                                                            |
| 1                    | J-19    | 500                 | 2.92                       | 1.39            | 19.06           | 0.42                            | 0.13            | 19.06           | 90                                                                                                            | 91                                                            |

# EXHIBIT 1-19

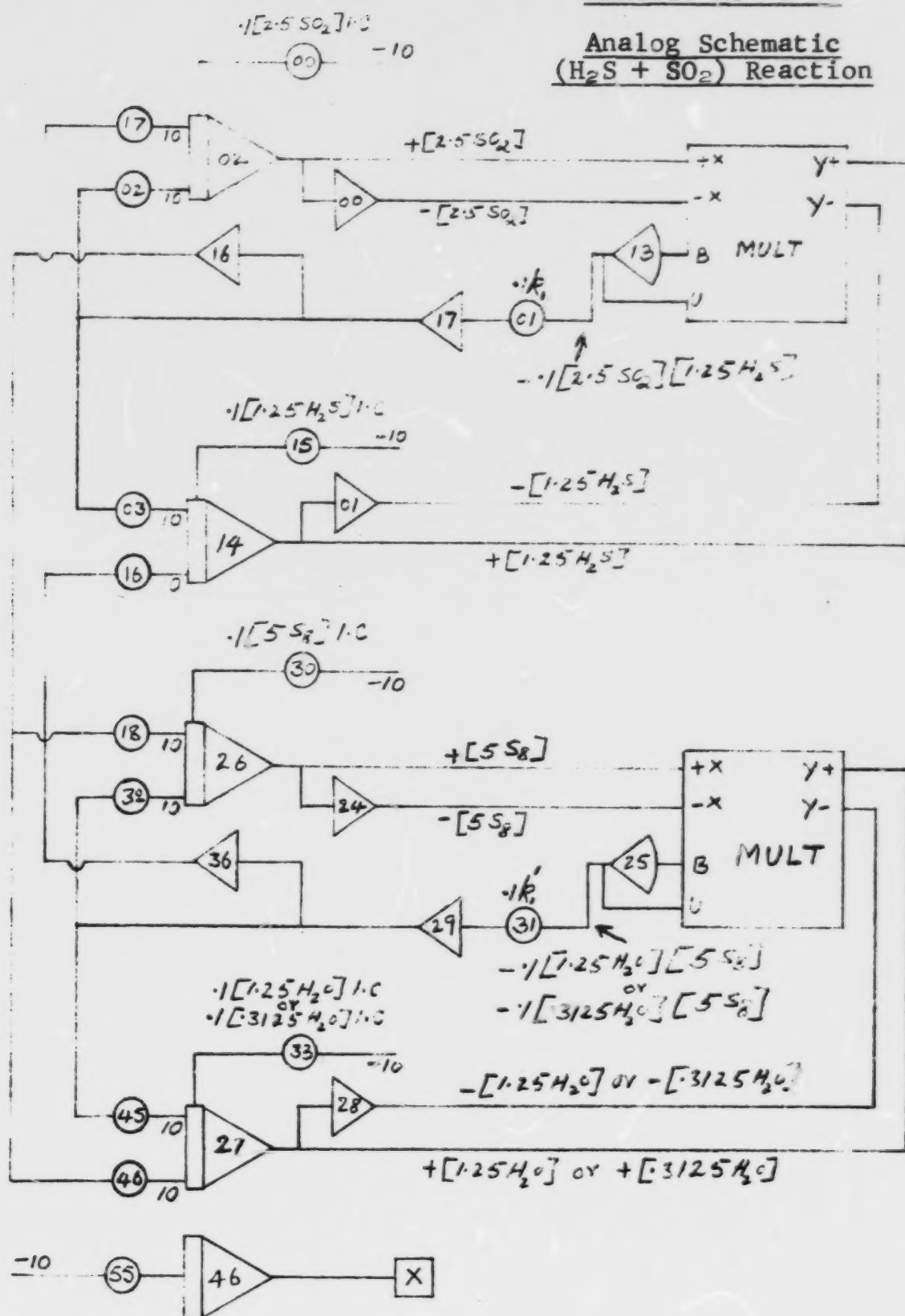
$K_e$ , Eqm. Const.

|                                                                                                  | 261°F<br>400°K        | 440°F<br>500°K        | 682°F<br>600°K        | 800°F<br>700°K        |
|--------------------------------------------------------------------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| $2 \text{ H}_2\text{S} + \text{SO}_2 \rightleftharpoons 3/8 \text{ S}_8 + 2 \text{ H}_2\text{C}$ | $6.9 \times 10^7$     | $8.87 \times 10^5$    | $1.86 \times 10^3$    | 95.5                  |
| $3 \text{ CO} + \text{SO}_2 \longrightarrow \text{COS} + 2 \text{ CO}_2$                         | $1.85 \times 10^{28}$ | $3.1 \times 10^{21}$  | $2.05 \times 10^{16}$ | $4.14 \times 10^{12}$ |
| $2 \text{ CCS} + \text{SO}_2 \longrightarrow 3/8 \text{ S}_8 + 2 \text{ CO}_2$                   | $3.44 \times 10^{16}$ | $9.86 \times 10^{11}$ | $7.83 \times 10^8$    | $6.97 \times 10^6$    |
| $\text{COS} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + \text{CO}_2$            | $2.23 \times 10^4$    | $2.86 \times 10^3$    | 719                   | 270                   |
| $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$                     | $1.55 \times 10^3$    | 138                   | 28.4                  | 9.55                  |
| $2 \text{ COS} \rightleftharpoons 2 \text{ CO} + 2/8 \text{ S}_8$                                | $0.33 \times 10^{-8}$ | $0.47 \times 10^{-6}$ | $0.13 \times 10^{-4}$ | $0.14 \times 10^{-3}$ |
| $2 \text{ COS} \rightleftharpoons \text{CS}_2 + \text{CO}_2$                                     | 0.225                 | 0.229                 | 0.231                 | 0.231                 |
| $2 \text{ H}_2 + \text{SO}_2 \longrightarrow 1/8 \text{ S}_8 + 2 \text{ H}_2\text{O}$            | $4.4 \times 10^{18}$  | $1.12 \times 10^{14}$ | $9.14 \times 10^{10}$ | $5.4 \times 10^8$     |
| $2 \text{ CS}_2 + \text{SO}_2 \longrightarrow 3/8 \text{ S}_8 + 2 \text{ COS}$                   | $6.78 \times 10^{17}$ | $1.89 \times 10^{13}$ | $1.81 \times 10^{10}$ | $1.31 \times 10^8$    |
| $\text{CS}_2 + 2 \text{ H}_2\text{O} \longrightarrow 2 \text{ H}_2\text{S} + \text{CO}_2$        | $2.21 \times 10^9$    | $3.57 \times 10^7$    | $2.24 \times 10^6$    | $3.16 \times 10^5$    |



EXHIBIT NO. 1-20

Analog Schematic  
(H<sub>2</sub>S + SO<sub>2</sub>) Reaction



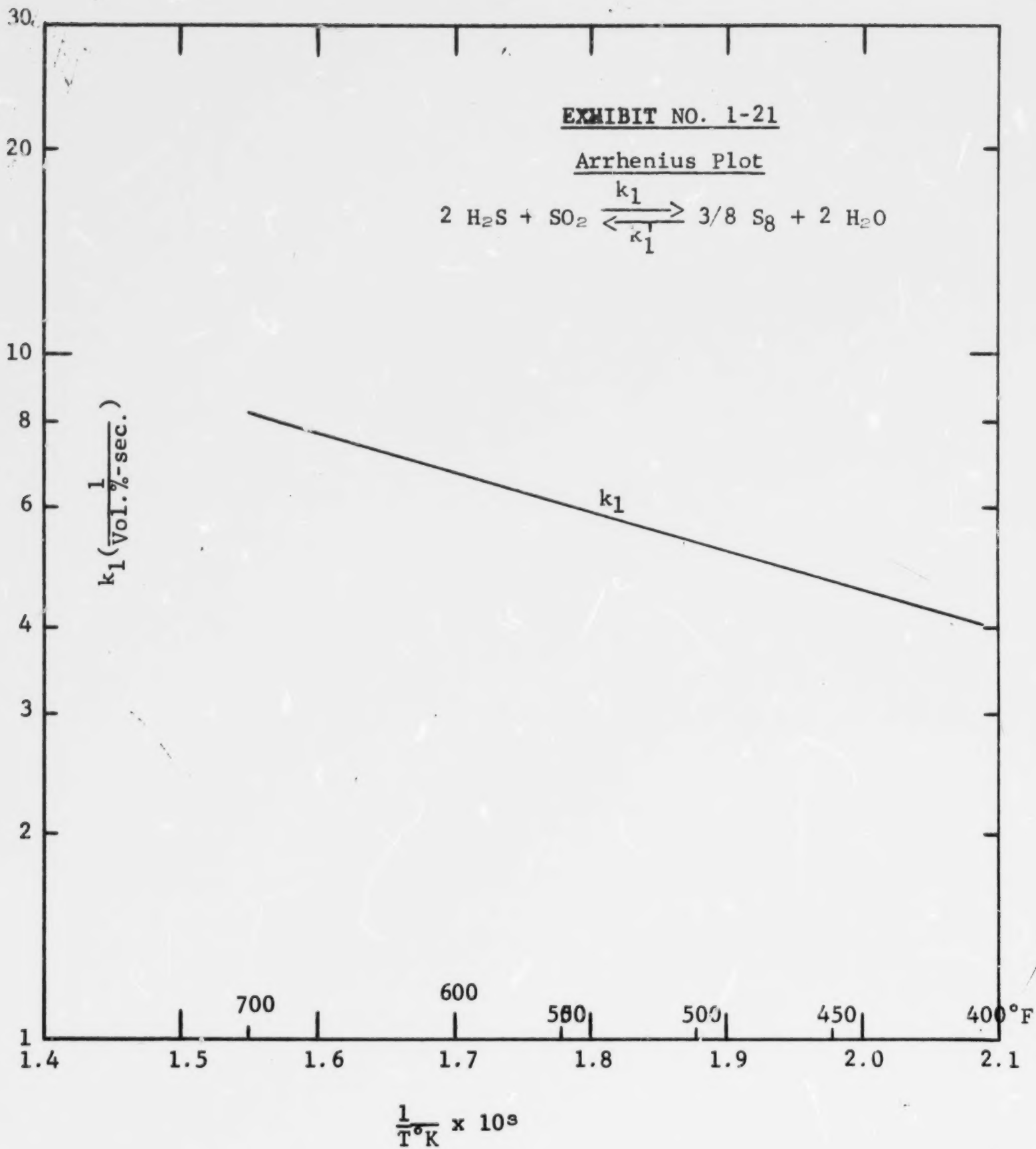
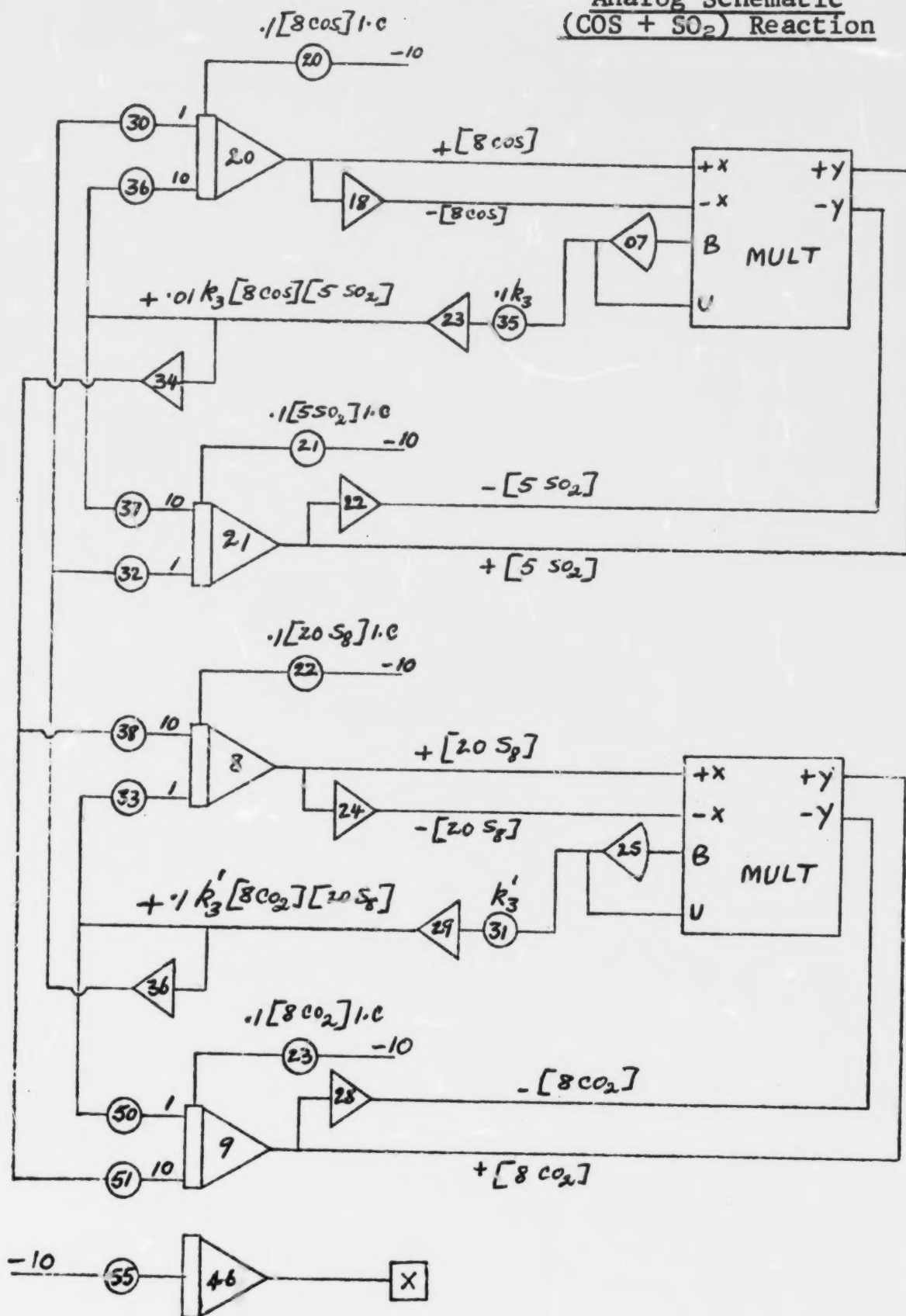


EXHIBIT NO. 1-22

Analog Schematic  
(COS + SO<sub>2</sub>) Reaction



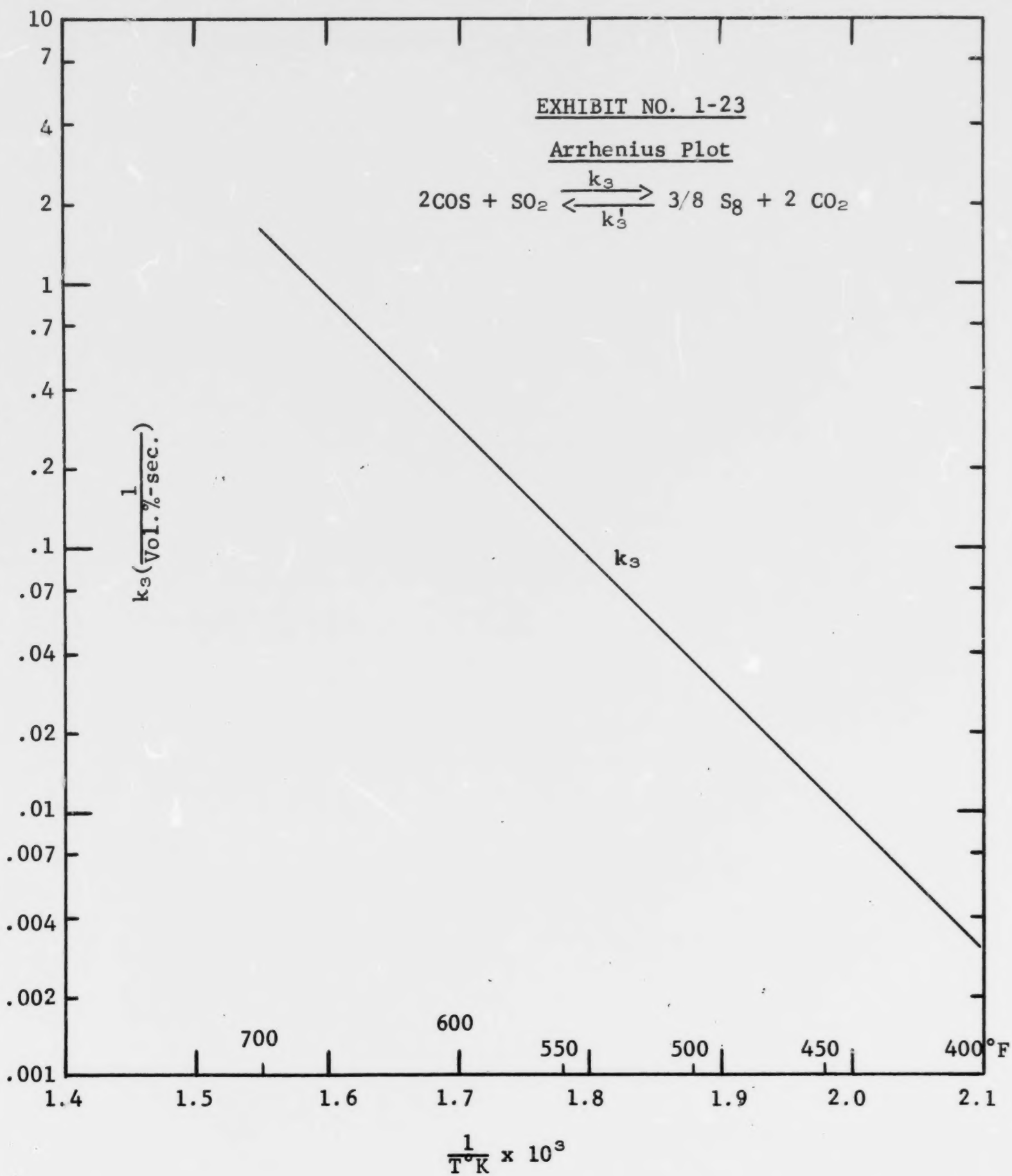




EXHIBIT NO. 1-24

Analog Schematic  
(COS + H<sub>2</sub>O) Reaction

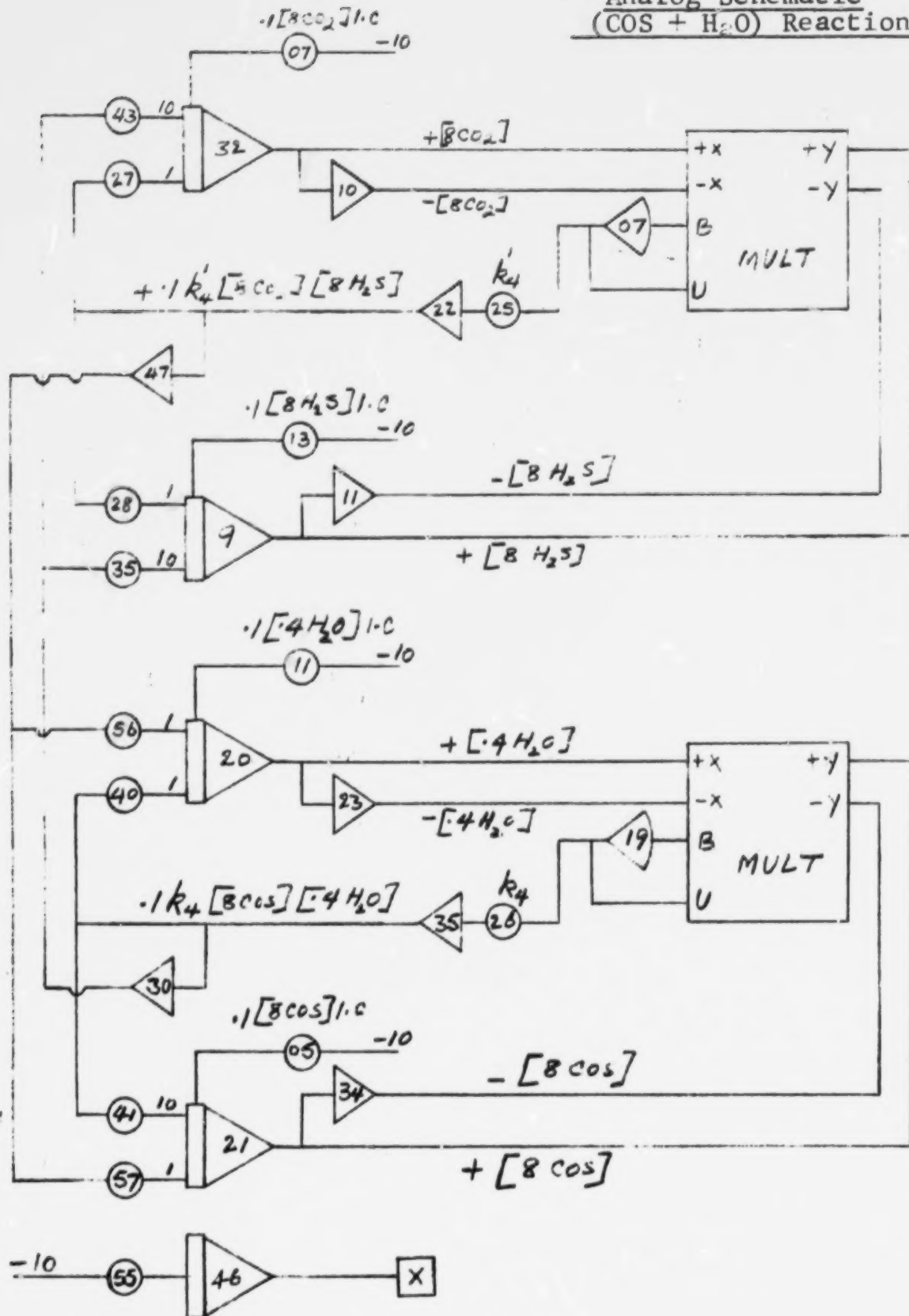
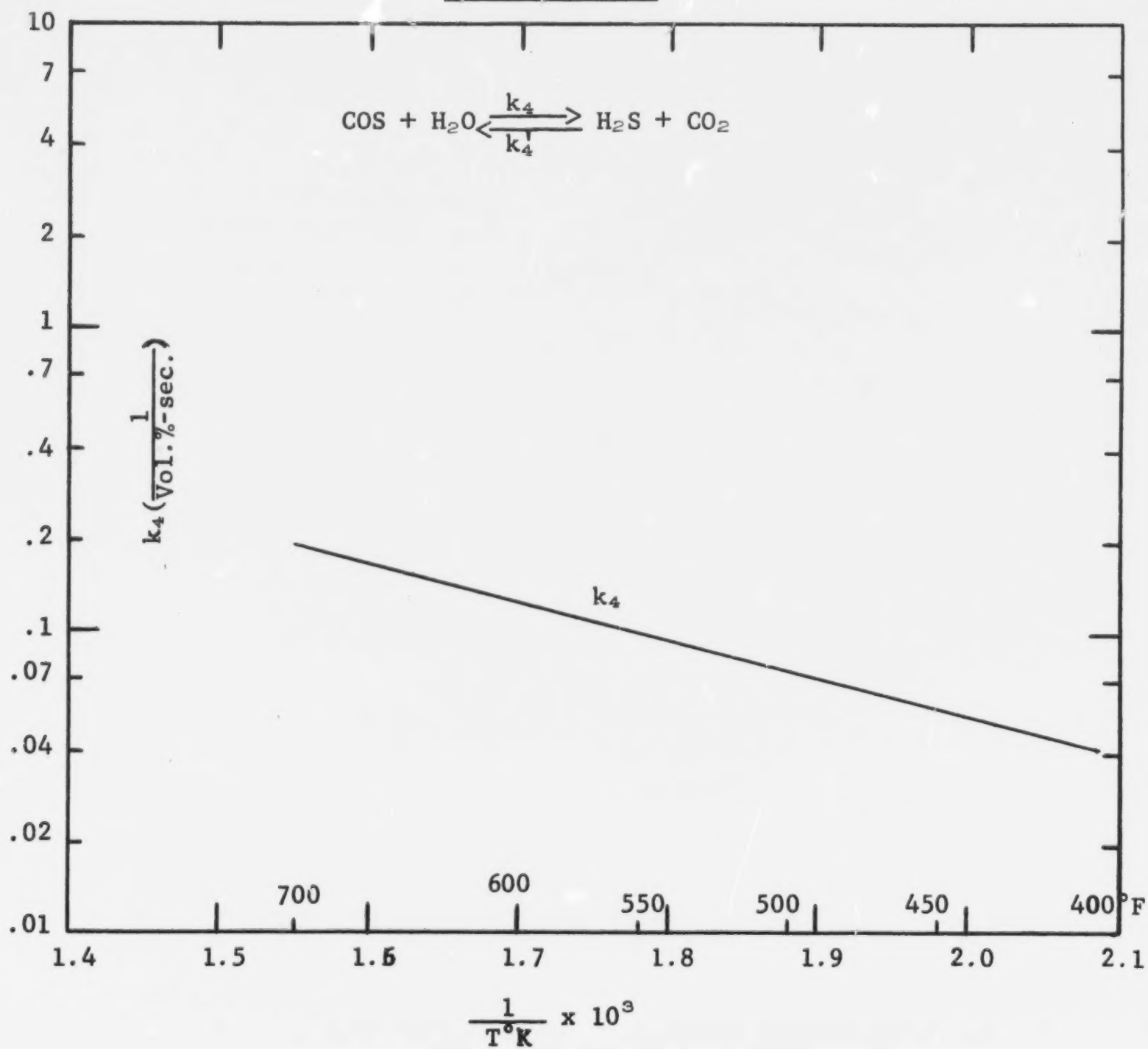
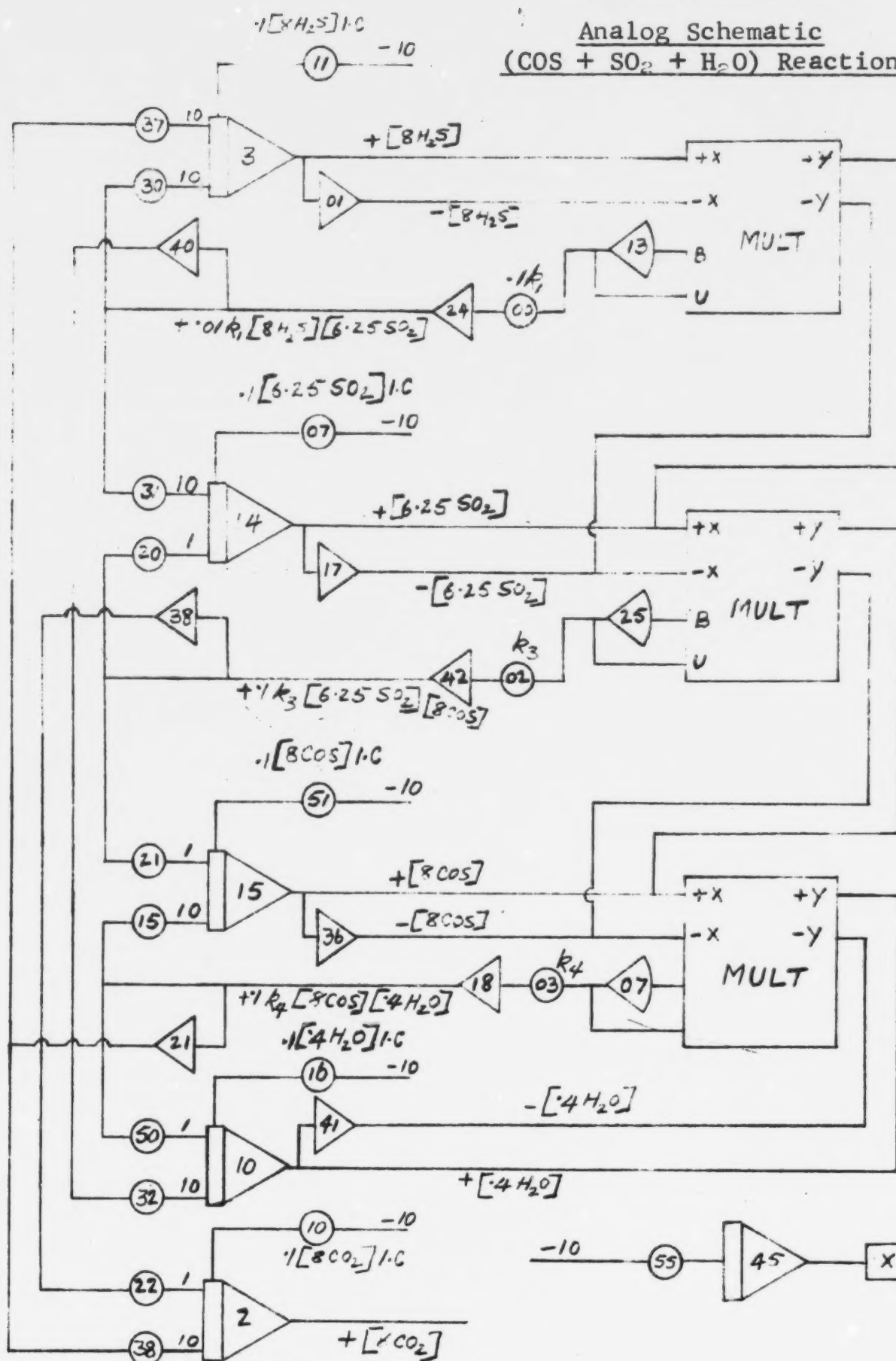


EXHIBIT NO. 1-25

Arrhenius Plot



Analog Schematic  
(COS + SO<sub>2</sub> + H<sub>2</sub>O) Reaction



Analog Schematic  
(CO + SO<sub>2</sub> + H<sub>2</sub>O) Reaction

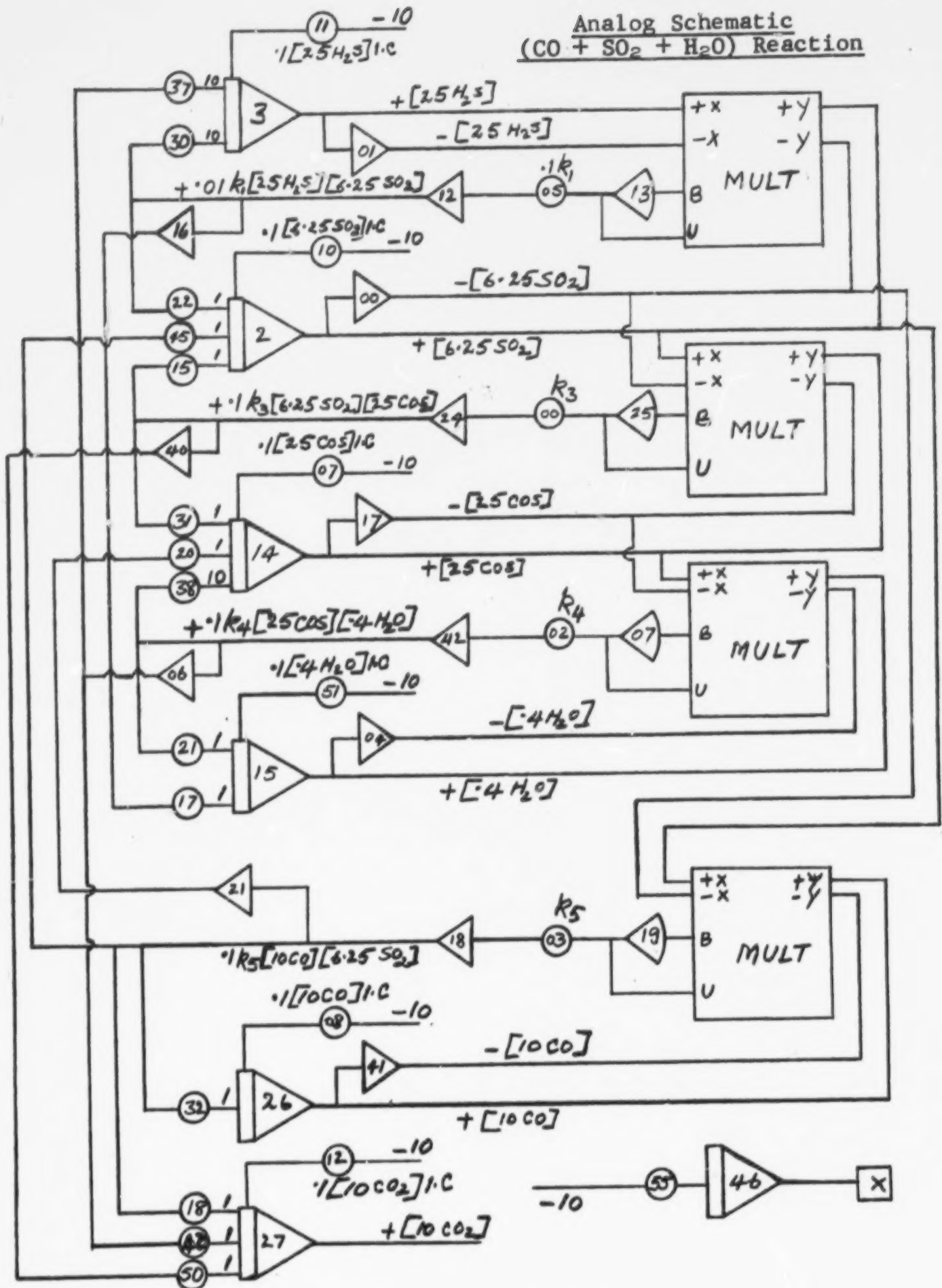




EXHIBIT NO. 1-28

Arrhenius Plot

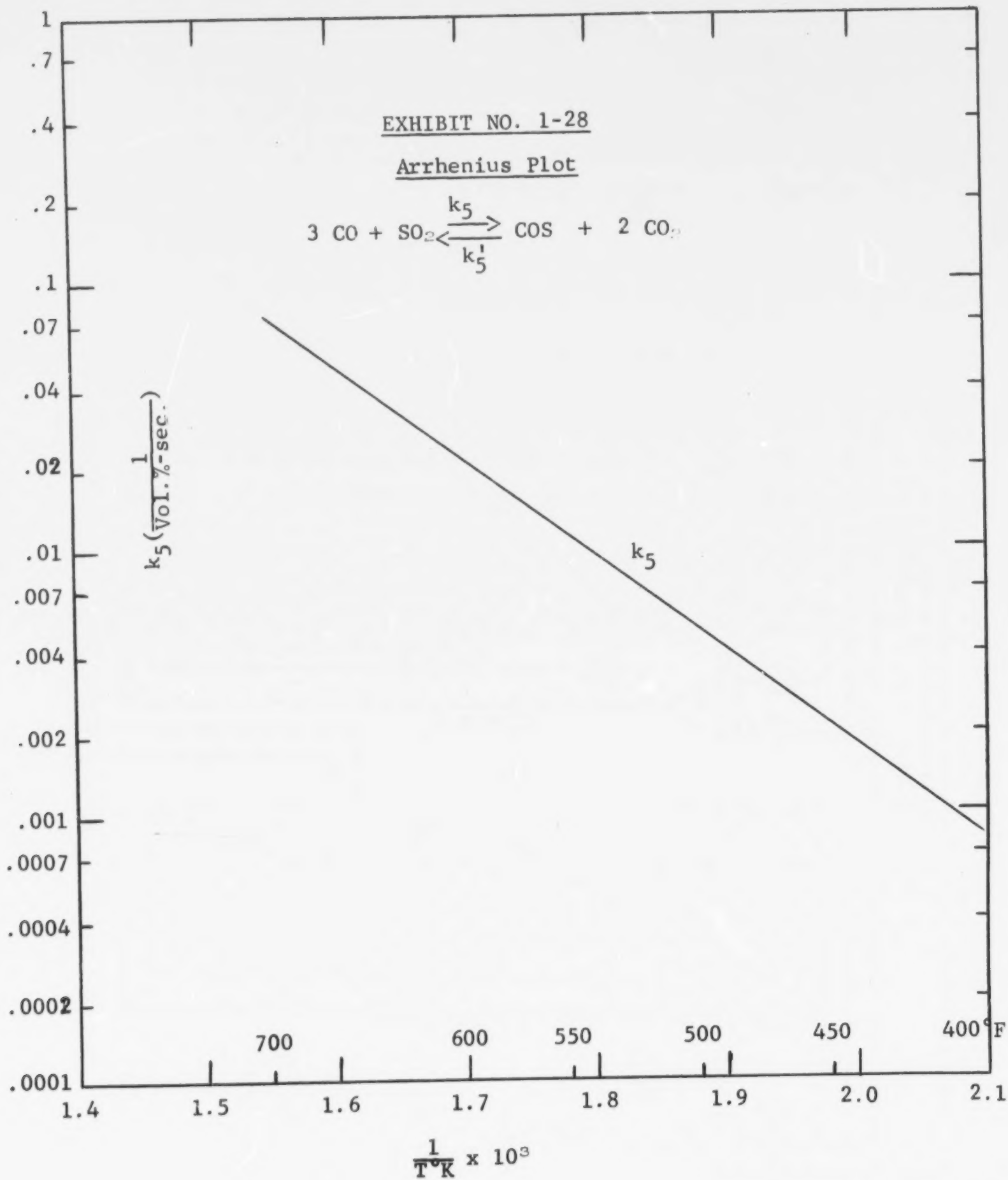
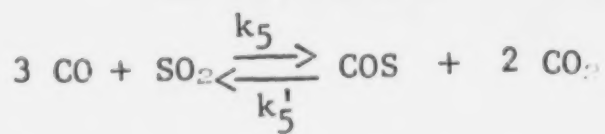


EXHIBIT NO. 1-29  
COMPARISON OF EXPERIMENTAL RESULTS WITH  
THOSE PREDICTED BY THE MODEL

400°F, 1/2 sec.

|       | Gas Composition - Volume % |      |                |                  |                 |                 |
|-------|----------------------------|------|----------------|------------------|-----------------|-----------------|
|       | CO                         | COS  | H <sub>2</sub> | H <sub>2</sub> S | SO <sub>2</sub> | CO <sub>2</sub> |
| Feed  | 0.98                       | 0.97 | 0.8            | 1.38             | 3.31            | 5.23            |
| Expt. | 0.98                       | 0.63 | 0.8            | 0.04             | 2.55            | 5.37            |
| Model | 0.98                       | 0.67 | 0.8            | 0.06             | 2.51            | 5.57            |

400°F, 1 sec.

|       |      |      |     |      |      |      |
|-------|------|------|-----|------|------|------|
| Feed  | 0.84 | 1.01 | 0.8 | 1.57 | 2.42 | 6.85 |
| Expt. | 0.84 | 0.62 | 0.8 | 0.0  | 1.33 | 7.27 |
| Model | 0.84 | 0.47 | 0.8 | 0.07 | 1.4  | 7.44 |

400°F, 2 sec.

|       |      |      |     |      |      |      |
|-------|------|------|-----|------|------|------|
| Feed  | 0.83 | 0.82 | 0.8 | 1.61 | 2.42 | 6.5  |
| Expt. | 0.83 | 0.13 | 0.8 | 0.03 | 1.08 | 6.84 |
| Model | 0.83 | 0.18 | 0.8 | 0.07 | 1.33 | 7.2  |

550°F, 1/2 sec.

|       |      |      |     |      |      |      |
|-------|------|------|-----|------|------|------|
| Feed  | 0.95 | 0.99 | 0.8 | 3.67 | 3.6  | 6.46 |
| Expt. | 0.95 | 0.39 | 0.8 | 0.31 | 1.42 | 6.99 |
| Model | 0.94 | 0.40 | 0.8 | 0.55 | 1.75 | 7.16 |

550°F, 1 sec.

|       |      |      |     |      |      |      |
|-------|------|------|-----|------|------|------|
| Feed  | 0.78 | 0.95 | 0.8 | 3.19 | 2.99 | 7.07 |
| Expt. | 0.78 | 0.23 | 0.8 | 0.40 | 1.19 | 7.66 |
| Model | 0.77 | 0.17 | 0.8 | 0.62 | 1.32 | 7.96 |

550°F, 2 sec.

|       |      |      |     |      |      |      |
|-------|------|------|-----|------|------|------|
| Feed  | 0.86 | 0.85 | 0.8 | 3.48 | 3.16 | 5.7  |
| Expt. | 0.81 | 0.0  | 0.8 | 0.3  | 0.97 | 6.48 |
| Model | 0.82 | 0.03 | 0.8 | 0.66 | 1.33 | 6.65 |

700°F, 1/2 sec.

|       |      |      |     |      |      |      |
|-------|------|------|-----|------|------|------|
| Feed  | 0.98 | 1.07 | 0.8 | 3.17 | 3.23 | 6.12 |
| Expt. | 0.85 | 0.08 | 0.8 | 1.05 | 1.96 | 6.89 |
| Model | 0.89 | 0.05 | 0.8 | 2.08 | 2.13 | 7.29 |

700°F, 1 sec.

|       |      |      |     |      |      |      |
|-------|------|------|-----|------|------|------|
| Feed  | 0.78 | 0.9  | 0.8 | 3.17 | 3.01 | 6.92 |
| Expt. | 0.68 | 0.04 | 0.8 | 1.28 | 1.48 | 7.71 |
| Model | 0.65 | 0.01 | 0.8 | 2.16 | 2.0  | 8.0  |

700°F, 2 sec.

|       |      |      |     |      |      |      |
|-------|------|------|-----|------|------|------|
| Feed  | 0.85 | 0.82 | 0.8 | 3.38 | 3.48 | 5.63 |
| Expt. | 0.54 | 0.0  | 0.8 | 1.47 | 1.33 | 6.91 |
| Model | 0.56 | 0.1  | 0.8 | 2.1  | 2.3  | 6.79 |

```

// JOB
// FOR
*IOCS(CARD, TYPEWRITER,1132PRINTER,KEYBOARD,DISK)
*EXTENDED PRECISION
*ONE WORD INTEGERS
*LIST ALL
  DEFINE FILE 11(50,100,U(111))
  REAL KF,KF1,KF2,KF3,KR,KR1,KR2,KR3,K(6),KP,M(11),MF(11)
  DIMENSION A(6,7)
  COMMON A
  CALL INP
  GO TO 20
1 ICT=1
  CALL DATSW(1,IPR1)
  GO TO (20,21),IPR1
200 FORMAT('(' TEMP ')')
20 WRITE(1,200)
  READ(6,10)T
  TK = (T-32.)/1.8+273.1
  KF = 61.66*EXP(-1305./TK)*1.E+04
  KF1 = 2.75*EXP(-2080./TK)*1.E+04
  KF2 = 2.09E+07*EXP(-10870./TK)*1.E+04
  KF3 = 813.*EXP(-6580./TK)*1.E+04
  ICT=2
21 CALL DATSW(2,IPR2)
  GO TO (22,23),IPR2
201 FORMAT('(' SO2 ')(' H2S ')(' S8 ')(' H2O ')(' CO2
1 ')(' COS ')')
22 WRITE(1,201)
  READ(6,10)SO2,H2S,S8,H2O,CO2,COS
601 FORMAT('(' CO ')(' H2 ')')
  WRITE(1,601)
  READ(6,10)CO,H2
  ERT = 100.-SO2 -H2S-S8-H2O-CO2-COS-CO-H2
  ICT=2
23 CALL DATSW(3,IPR3)
  GO TO(24,50),IPR3
10 FORMAT(1X,6(F10.2,2X))
202 FORMAT('(' TIME ')','(' INTG INT ')')
24 WRITE(1,202)
  READ(6,10)TIME,A11
  ICT=2
50 GO TO (25,51),ICT
51 DO 300 I=1,11
300 M (I)=0.0
  M(1) =SO2
  M(2) =H2S
  M(5) =S8
  M(6) =H2O
  M(7) =CO2
  M(8) =COS
  M(9)=CO
  M(10)=H2
  M(11)=ERT
  READ(11'1)N,NC,NJJ
  WRITE(11'N+3)M
  CALL VARB
  DO 361 I=1,11
361 MF(I)=M (I)

```

EXHIBIT NO. 1-30

## EXHIBIT NO. 1-30 (Continued)

```

CALL EQ (T,MF,K)
MF(5) = MF(5)+MF(4)*6./8.+MF(3)*2./8.
MF(4)=0.0
MF(3)=0.
TOT = 0.0
DO 362 I=1,11
362 TOT = TOT+MF(I)
EQK = MF(6)**2*MF(5)**(3./8.)/(MF(1)/(MF(2)**2)*(TOT)**(5./8.))
KP = EQK*MF(2)*MF(5)**(5./8.)/(MF(6)*TOT**((5./8.)))
KR=KF/KP
EQK1 = MF(2)*MF(7)/(MF(8)*MF(6))
KR1 = KF1/EQK1
EQK2 = (MF(7)**2*MF(5)**(3./8.))/(MF(1)*MF(8)**2*TOT**((5./8.))
KP = EQK2*MF(8)*MF(5)**(5./8.)/(MF(7)*TOT**((5./8.)))
KR2 = KF2/KP
EQK3 = (MF(8)*MF(7)**2*TOT)/(MF(9)**3*MF(1))
KP=EQK3*MF(9)/MF(7)
KR3=KF3/KP
DO 364 I=1,11
364 MF(I)=MF(I)/TOT*100.
WRITE(3,101)
WRITE(3,106) T,EQK,EQK1,EQK2,EQK3,KF,KF1,KF2,KF3,KR,KR1,KR2,KR3
WRITE(3,321)
WRITE(3,103) MF(1),MF(2),MF(5),MF(6),MF(7),MF(8),MF(9),MF(10),MF(
11)
321 FORMAT(1X,'***TIME***',7X,'S02',7X,'H2S',8X,'S8',7X,'H2O',7X,'CO2',
17X,'COS',8X,'CO',8X,'H2',5X,'INERT')
RES=0.0
WRITE(3,102) RES,S02,H2S,S8,H2O,CO2,COS,CO,H2,ERT
25 TIM1=TIME
CALL RKGS (M,MF,T,TIM1,RES,KF,KF1,KF2,KF3,KR,KR1,KR2,KR3,ALL)
S=0.0
DO 60 I=1,11
60 S=S+MF(I)
DO 61 I=1,11
61 IF(I)=MF(I)/S*100.
RES=RES+.00001
WRITE(3,100) RES,MF(1),MF(2),MF(5),MF(6),MF(7),MF(8),MF(9),MF(11)
RES=RES-.00001
GO TO 1
100 FORMAT(1X,8F10.4,10X,F10.4)
101 FORMAT(1H1)
102 FORMAT(1X,10F10.4)
106 FORMAT(1X,'TEMP.
11X,'FORWARD K',4E13.5/1X,'BACKWARD K',4E13.5//)
103 FORMAT(1X,4X,'EQUIL.',9F10.4/)
END

```

## VARIABLE ALLOCATIONS

|      |        |     |        |      |        |     |        |      |        |     |        |      |        |      |        |      |        |      |        |
|------|--------|-----|--------|------|--------|-----|--------|------|--------|-----|--------|------|--------|------|--------|------|--------|------|--------|
| A    | = 7FFD | KF  | = 0008 | KF1  | = 000B | KF2 | = 000E | KF3  | = 0011 | KR  | = 0014 | KR1  | = 0017 | KR2  | = 001A | KR3  | = 001D | K    | = 002F |
| KP   | = 0032 | M   | = 0053 | MF   | = 0074 | T   | = 0077 | TK   | = 007A | SJ2 | = 007D | M25  | = 0080 | S8   | = 0083 | T2J  | = 0086 | CU2  | = 0089 |
| ECOS | = 008C | CO  | = 008F | M2   | = 0092 | ERT | = 0095 | TIME | = 0098 | ALL | = 009B | TUT  | = 009E | EWK  | = 00A1 | EWK1 | = 00A4 | LJK2 | = 00A7 |
| EQK3 | = 00AA | RES | = 00AD | TI41 | = 00B0 | S   | = 00B3 | ILL  | = 00C2 | ICI | = 00C5 | IPK1 | = 00C4 | IPK2 | = 00C5 | IPK3 | = 00C6 | I    | = 00C7 |
| N    | = 00CH | NC  | = 00C9 | NJJ  | = 00CA |     |        |      |        |     |        |      |        |      |        |      |        |      |        |

## STATEMENT ALLOCATIONS

|     |        |     |        |     |        |    |        |     |        |     |        |     |        |     |        |     |        |     |        |
|-----|--------|-----|--------|-----|--------|----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|
| 200 | = 0115 | 201 | = 011D | 601 | = 0143 | 10 | = 0151 | 202 | = 0157 | 321 | = 0166 | 100 | = 0191 | 104 | = 0197 | 402 | = 019A | 106 | = 019E |
|-----|--------|-----|--------|-----|--------|----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|-----|--------|

| TEMP.      | 0.4000E 03 DEG. F | 0.7226E 13   | 0.8225E 23   |
|------------|-------------------|--------------|--------------|
| EQUIL. K   | 0.39510E 06       | 0.42765E 04  | 0.79999E 01  |
| FORWARD K  | 0.40000E 05       | 0.35000E 03  | 0.93729E -13 |
| BACKWARD K | 0.51029E 03       | 0.81841E -01 | 0.74576E -04 |

| ***TIME***                      | S02         | H2S    | S8          | H2O         | CU2    | CUS         | CU     | MZ          | INERT   |
|---------------------------------|-------------|--------|-------------|-------------|--------|-------------|--------|-------------|---------|
| EQUIL.                          | 1.3218      | 0.1163 | 0.5383      | 22.3962     | 7.2876 | 0.0000      | 0.0000 | 0.0000      | 60.3355 |
| 0.0000                          | 3.3100      | 1.3800 | 0.0000      | 20.0000     | 5.2300 | 0.9700      | 0.9800 | 0.8000      | 61.3300 |
| 0.1000                          | 2.6861      | 0.1820 | 0.2387      | 21.2830     | 5.3214 | 0.9039      | 0.9832 | 0.8000      | 61.5981 |
| 0.2000                          | 2.5996      | 0.0731 | 0.2718      | 21.4038     | 5.3913 | 0.8380      | 0.9831 | 0.8000      | 61.6353 |
| 0.3000                          | 2.5629      | 0.0606 | 0.2858      | 21.4213     | 5.4548 | 0.7766      | 0.9827 | 0.8000      | 61.6511 |
| 0.4000                          | 2.5336      | 0.0589 | 0.2969      | 21.4269     | 5.5135 | 0.7196      | 0.9823 | 0.8000      | 61.6638 |
| 0.5000                          | 2.5071      | 0.0585 | 0.3070      | 21.4310     | 5.5680 | 0.6669      | 0.9819 | 0.8000      | 61.6752 |
| 0.6000                          | 2.4825      | 0.0583 | 0.3163      | 21.4346     | 5.6185 | 0.6179      | 0.9814 | 0.8000      | 61.6858 |
| 0.7000                          | 2.4598      | 0.0580 | 0.3250      | 21.4380     | 5.6653 | 0.5726      | 0.9810 | 0.8000      | 61.6950 |
| 0.8000                          | 2.4386      | 0.0578 | 0.3330      | 21.4411     | 5.7087 | 0.5306      | 0.9805 | 0.8000      | 61.7048 |
| 0.9000                          | 2.4191      | 0.0576 | 0.3404      | 21.4440     | 5.7490 | 0.4916      | 0.9801 | 0.8000      | 61.7132 |
| TOL. ON EQUIL. CONSTANT NOT MET |             |        |             |             |        |             |        |             |         |
| 0.17866E-24                     | 0.25532E 15 |        | 0.21649E 03 | 0.65435E 12 |        | 0.27234E 13 |        | 0.22099E 21 |         |
| 0.17876E-24                     | 0.25525E 15 |        | 0.22357E 03 | 0.69766E 12 |        | 0.27234E 13 |        | 0.22100E 21 |         |



TEMP. 0.40000E 03 DEG. F  
 EQUIL. K 0.39511E 06 0.42764E 04 0.72256E 13 0.98742E 23  
 FORWARD K 0.40000E 05 0.35000E 03 0.25000E 02 0.79999E 01  
 BACKWARD K 0.31527E 03 0.81844E-01 0.46078E-04 0.50642E-13

| ***TIME*** | SO2    | H2S    | S8     | H2O     | CO2    | CUS    | CU     | H2     | INERT   |
|------------|--------|--------|--------|---------|--------|--------|--------|--------|---------|
| EQUIL.     | 0.4913 | 0.1914 | 0.5295 | 22.5398 | 8.2668 | 0.0000 | 0.0000 | 0.0000 | 67.9809 |
| 0.0000     | 2.4200 | 1.6100 | 0.0000 | 20.0000 | 6.5000 | 0.8200 | 0.8300 | 0.8000 | 67.0200 |
| 0.1000     | 1.7756 | 0.3672 | 0.2452 | 21.3310 | 6.5857 | 0.7645 | 0.8329 |        | 67.2940 |
| 0.2000     | 1.6380 | 0.1458 | 0.2976 | 21.5713 | 6.6479 | 0.7090 | 0.8333 |        | 67.3526 |
| 0.3000     | 1.5858 | 0.0929 | 0.3174 | 21.6314 | 6.7028 | 0.6569 | 0.8333 |        | 67.3748 |
| 0.4000     | 1.5546 | 0.0788 | 0.3293 | 21.6498 | 6.7530 | 0.6085 | 0.8331 |        | 67.3881 |
| 0.5000     | 1.5300 | 0.0746 | 0.3386 | 21.6574 | 6.7994 | 0.5636 | 0.8329 |        | 67.3986 |
| 0.6000     | 1.5084 | 0.0730 | 0.3468 | 21.6620 | 6.8423 | 0.5220 | 0.8328 |        | 67.4078 |
| 0.7000     | 1.4887 | 0.0720 | 0.3542 | 21.6656 | 6.8820 | 0.4834 | 0.8326 |        | 67.4162 |
| 0.8000     | 1.4705 | 0.0713 | 0.3611 | 21.6689 | 6.9189 | 0.4477 | 0.8324 |        | 67.4240 |
| 0.9000     | 1.4536 | 0.0707 | 0.3675 | 21.6718 | 6.9530 | 0.4147 | 0.8322 |        | 67.4312 |
| 1.0000     | 1.4380 | 0.0701 | 0.3734 | 21.6745 | 6.9847 | 0.3840 | 0.8319 |        | 67.4378 |
| 1.1000     | 1.4235 | 0.0696 | 0.3789 | 21.6770 | 7.0140 | 0.3557 | 0.8317 |        | 67.4440 |
| 1.2000     | 1.4101 | 0.0691 | 0.3840 | 21.6794 | 7.0412 | 0.3294 | 0.8315 |        | 67.4498 |
| 1.3000     | 1.3977 | 0.0686 | 0.3887 | 21.6816 | 7.0664 | 0.3051 | 0.8313 |        | 67.4551 |
| 1.4000     | 1.3861 | 0.0682 | 0.3931 | 21.6836 | 7.0897 | 0.2826 | 0.8311 |        | 67.4600 |
| 1.5000     | 1.3754 | 0.0677 | 0.3971 | 21.6855 | 7.1114 | 0.2617 | 0.8309 |        | 67.4646 |
| 1.6000     | 1.3655 | 0.0673 | 0.4008 | 21.6873 | 7.1314 | 0.2424 | 0.8306 |        | 67.4688 |
| 1.7000     | 1.3563 | 0.0670 | 0.4043 | 21.6889 | 7.1500 | 0.2245 | 0.8304 |        | 67.4728 |
| 1.8000     | 1.3478 | 0.0666 | 0.4075 | 21.6905 | 7.1672 | 0.2079 | 0.8302 |        | 67.4764 |
| 1.9000     | 1.3399 | 0.0663 | 0.4105 | 21.6919 | 7.1832 | 0.1926 | 0.8300 |        | 67.4798 |
| 2.0000     | 1.3325 | 0.0660 | 0.4133 | 21.6932 | 7.1980 | 0.1784 | 0.8297 |        | 67.4829 |
| 2.1000     | 1.3257 | 0.0657 | 0.4158 | 21.6944 | 7.2118 | 0.1652 | 0.8295 |        | 67.4859 |

TOL. ON EQUIL. CONSTANT NOT MET  
 0.17866E-24 0.25532E 15 0.21649E 03 0.65435E 12 0.27234E 13 0.22099E 21  
 0.17914E-24 0.25498E 15 0.21074E 03 0.61924E 12 0.27234E 13 0.22099E 21

TEMP. 0.40000E 03 DEG. F 0.72256E 13 0.82573E 23  
 EQUIL. K 0.39509E 06 C.42764E 04 0.25000E 02 0.79999E 01  
 FORWARD K 0.40000E 05 0.35000E 03 0.62482E-04 0.81898E-13  
 BACKWARD K 0.42752E 03 0.81843E-01 0.62482E-04 0.81898E-13

| ***TIME*** | SO2    | H2S    | S8     | H2O     | CO2    | COS    | CU     | H2     | INERT   |
|------------|--------|--------|--------|---------|--------|--------|--------|--------|---------|
| EQUIL.     | 1.0220 | 0.1348 | 0.5713 | 22.5727 | 8.7946 | 0.0000 | 0.0000 | 0.0000 | 66.9042 |
| 0.0000     | 3.1000 | 1.5600 | 0.0000 | 20.0000 | 6.7000 | 0.9800 | 0.9800 | 0.8000 | 55.8800 |
| 0.1000     | 2.4124 | 0.2360 | 0.2628 | 21.4184 | 6.8008 | 0.9134 | 0.9836 |        | 66.1687 |
| 0.2000     | 2.3070 | 0.0901 | 0.3031 | 21.5788 | 6.8734 | 0.8465 | 0.9837 |        | 66.2130 |
| 0.3000     | 2.2655 | 0.0691 | 0.3188 | 21.6055 | 6.9384 | 0.7841 | 0.9834 |        | 66.2305 |
| 0.4000     | 2.2349 | 0.0657 | 0.3305 | 21.6132 | 6.9984 | 0.7262 | 0.9831 |        | 66.2434 |
| 0.5000     | 2.2076 | 0.0648 | 0.3408 | 21.6178 | 7.0539 | 0.6725 | 0.9827 |        | 66.2548 |
| 0.6000     | 2.1826 | 0.0643 | 0.3503 | 21.6218 | 7.1054 | 0.6228 | 0.9824 |        | 66.2654 |
| 0.7000     | 2.1594 | 0.0639 | 0.3592 | 21.6254 | 7.1531 | 0.5767 | 0.9820 |        | 66.2752 |
| 0.8000     | 2.1379 | 0.0635 | 0.3673 | 21.6287 | 7.1973 | 0.5341 | 0.9816 |        | 66.2843 |
| 0.9000     | 2.1180 | 0.0632 | 0.3749 | 21.6318 | 7.2382 | 0.4946 | 0.9813 |        | 66.2927 |
| 1.0000     | 2.0995 | 0.0629 | 0.3819 | 21.6347 | 7.2762 | 0.4581 | 0.9809 |        | 66.3005 |
| 1.1000     | 2.0823 | 0.0626 | 0.3884 | 21.6373 | 7.3114 | 0.4242 | 0.9805 |        | 66.3077 |
| 1.2000     | 2.0665 | 0.0623 | 0.3944 | 21.6398 | 7.3440 | 0.3929 | 0.9801 |        | 66.3144 |
| 1.3000     | 2.0517 | 0.0620 | 0.4000 | 21.6421 | 7.3743 | 0.3638 | 0.9797 |        | 66.3206 |
| 1.4000     | 2.0381 | 0.0617 | 0.4051 | 21.6443 | 7.4023 | 0.3369 | 0.9793 |        | 66.3264 |
| 1.5000     | 2.0254 | 0.0615 | 0.4099 | 21.6463 | 7.4283 | 0.3121 | 0.9789 |        | 66.3318 |
| 1.6000     | 2.0137 | 0.0613 | 0.4143 | 21.6481 | 7.4524 | 0.2890 | 0.9785 |        | 66.3367 |
| 1.7000     | 2.0028 | 0.0611 | 0.4184 | 21.6498 | 7.4747 | 0.2677 | 0.9781 |        | 66.3413 |
| 1.8000     | 1.9927 | 0.0609 | 0.4222 | 21.6514 | 7.4955 | 0.2479 | 0.9777 |        | 66.3456 |
| 1.9000     | 1.9834 | 0.0607 | 0.4257 | 21.6529 | 7.5147 | 0.2296 | 0.9773 |        | 66.3495 |
| 2.0000     | 1.9747 | 0.0605 | 0.4290 | 21.6543 | 7.5325 | 0.2127 | 0.9768 |        | 66.3533 |
| 2.1000     | 1.9667 | 0.0604 | 0.4320 | 21.6555 | 7.5490 | 0.1970 | 0.9764 |        | 66.3567 |
| 2.2000     | 1.9592 | 0.0602 | 0.4348 | 21.6567 | 7.5644 | 0.1825 | 0.9760 |        | 66.3599 |
| 2.3000     | 1.9522 | 0.0601 | 0.4374 | 21.6578 | 7.5786 | 0.1691 | 0.9756 |        | 66.3628 |
| 2.4000     | 1.9458 | 0.0600 | 0.4398 | 21.6588 | 7.5918 | 0.1567 | 0.9752 |        | 66.3656 |
| 2.5000     | 1.9398 | 0.0599 | 0.4420 | 21.6598 | 7.6041 | 0.1451 | 0.9748 |        | 66.3681 |
| 2.6000     | 1.9343 | 0.0598 | 0.4441 | 21.6607 | 7.6155 | 0.1345 | 0.9743 |        | 66.3705 |
| 2.7000     | 1.9292 | 0.0597 | 0.4460 | 21.6615 | 7.6261 | 0.1246 | 0.9739 |        | 66.3727 |
| 2.8000     | 1.9244 | 0.0596 | 0.4478 | 21.6622 | 7.6359 | 0.1155 | 0.9735 |        | 66.3747 |
| 2.9000     | 1.9199 | 0.0595 | 0.4494 | 21.6629 | 7.6450 | 0.1070 | 0.9731 |        | 66.3765 |
| 3.0000     | 1.9158 | 0.0594 | 0.4510 | 21.6636 | 7.6535 | 0.0992 | 0.9726 |        | 66.3784 |
| 3.1000     | 1.9120 | 0.0593 | 0.4524 | 21.6642 | 7.6614 | 0.0920 | 0.9722 |        | 66.3800 |
| 3.2000     | 1.9084 | 0.0593 | 0.4537 | 21.6648 | 7.6687 | 0.0853 | 0.9718 |        | 66.3816 |

TEMP. 0.55000E 03 DEG. F 0.11017E 11 0.13061E 19  
 EQUIL. K 0.80092E 04 0.11728E 04 0.78000E 03 0.65000E 02  
 FORWARD K 0.60000E 05 0.67000E 03 0.36862E-01 0.33899E-09  
 BACKWARD K 0.33256E 04 0.57126E 00

\*\*\*TIME\*\*\*  
 EQUIL. S02 H2S S8 H2O CU2 CUS CU H2 INERT  
 0.0000 0.9537 1.1018 0.7953 23.8378 8.5609 0.0003 0.0000 0.0000 64.7497  
 0.1000 3.6000 0.5764 0.0000 20.0000 6.4600 0.9900 0.9200 63.5300  
 0.2000 1.9834 0.5029 0.6195 23.3383 6.7017 0.8287 0.9553 64.1869  
 0.3000 1.8753 0.5175 0.6606 23.4282 6.8525 0.6877 0.9524 64.2312  
 0.4000 1.8231 0.5342 0.6802 23.4216 6.9750 0.5712 0.9492 64.2527  
 0.5000 1.7819 0.5487 0.6956 23.4113 7.0767 0.4749 0.9461 64.2697  
 0.6000 1.7479 0.5487 0.7082 23.4020 7.1613 0.3952 0.9430 64.2837

TEMP. 0.55000E 03 DEG. F 0.11022E 11 0.13052E 19  
 EQUIL. K 0.80129E 04 0.11728E 04 0.78000E 03 0.65000E 02  
 FORWARD K 0.60000E 05 0.67000E 03 0.37130E-01 0.29930E-09  
 BACKWARD K 0.33497E 04 0.57126E 00

| ***TIME*** | SO2    | H2S    | S8     | H2O     | CO2    | CUS    | CU     | MZ     | INERT   |
|------------|--------|--------|--------|---------|--------|--------|--------|--------|---------|
| EQUIL.     | 0.7265 | 1.1381 | 0.6665 | 23.1965 | 8.9444 | 0.0003 | 0.0000 | 0.0001 | 65.2771 |
| 0.0000     | 2.9900 | 3.1900 | 0.0000 | 20.0000 | 7.0700 | 0.9500 | 0.7800 | 0.8000 | 64.2200 |
| 0.1000     | 1.6402 | 0.6266 | 0.5154 | 22.7628 | 7.2908 | 0.8011 | 0.7836 | 0.8000 | 64.7723 |
| 0.2000     | 1.5247 | 0.5267 | 0.5592 | 22.8798 | 7.4293 | 0.6710 | 0.7817 | 0.8000 | 64.8197 |
| 0.3000     | 1.4754 | 0.5387 | 0.5777 | 22.8752 | 7.5429 | 0.5623 | 0.7797 | 0.8000 | 64.8400 |
| 0.4000     | 1.4383 | 0.5569 | 0.5917 | 22.8625 | 7.6377 | 0.4716 | 0.7776 | 0.8000 | 64.8554 |
| 0.5000     | 1.4078 | 0.5734 | 0.6031 | 22.8506 | 7.7173 | 0.3958 | 0.7756 | 0.8000 | 64.8681 |
| 0.6000     | 1.3824 | 0.5877 | 0.6125 | 22.8400 | 7.7841 | 0.3324 | 0.7736 | 0.8000 | 64.8787 |
| 0.7000     | 1.3611 | 0.6001 | 0.6204 | 22.8308 | 7.8403 | 0.2794 | 0.7716 | 0.8000 | 64.8875 |
| 0.8000     | 1.3434 | 0.6108 | 0.6269 | 22.8228 | 7.8876 | 0.2350 | 0.7697 | 0.8000 | 64.8949 |
| 0.9000     | 1.3284 | 0.6200 | 0.6323 | 22.8159 | 7.9276 | 0.1979 | 0.7677 | 0.8000 | 64.9012 |
| 1.0000     | 1.3159 | 0.6279 | 0.6369 | 22.8099 | 7.9615 | 0.1667 | 0.7658 | 0.8000 | 64.9065 |
| 1.1000     | 1.3053 | 0.6347 | 0.6407 | 22.8048 | 7.9901 | 0.1405 | 0.7639 | 0.8000 | 64.9110 |

TEMP. 0.55000E 03 DEG. F 0.11728E 04 0.11019E 11 0.13043E 19  
 EQUIL. K 0.80104E 04 0.67000E 03 0.78000E 03 0.55000E 02  
 FORWARD K 0.60000E 05 0.57123E 00 0.42539E-01 0.37038E-09  
 BACKWARD K 0.38380E 04

| ***TIME***                      | SQ2         | H2S         | S8          | H2O         | CO2         | CUS    | CU     | M2     | INERT   |
|---------------------------------|-------------|-------------|-------------|-------------|-------------|--------|--------|--------|---------|
| EQUIL.                          | 1.1258      | 0.9899      | 0.7383      | 23.5753     | 8.1742      | 0.0002 | 0.0000 | 0.0001 | 65.3967 |
| 0.0000                          | 3.6000      | 3.3300      | 0.0000      | 20.0000     | 6.2000      | 0.9500 | 0.8800 | 0.8000 | 64.2400 |
| 0.1000                          | 2.1317      | 0.5259      | 0.5627      | 23.0232     | 6.4269      | 0.7945 | 0.8839 | 0.8000 | 64.9434 |
| 0.2000                          | 2.0364      | 0.4723      | 0.5988      | 23.0911     | 6.5701      | 0.6593 | 0.8808 | 0.8000 | 64.8828 |
| 0.3000                          | 1.9869      | 0.4875      | 0.6174      | 23.0834     | 6.6876      | 0.5476 | 0.8776 | 0.8000 | 64.9034 |
| 0.4000                          | 1.9472      | 0.5031      | 0.6322      | 23.0738     | 6.7852      | 0.4552 | 0.8745 | 0.8000 | 64.9200 |
| 0.5000                          | 1.9144      | 0.5167      | 0.6443      | 23.0652     | 6.8664      | 0.3788 | 0.8713 | 0.8000 | 64.9337 |
| 0.6000                          | 1.8872      | 0.5283      | 0.6544      | 23.0578     | 6.9342      | 0.3155 | 0.8682 | 0.8000 | 64.9452 |
| 0.7000                          | 1.8646      | 0.5382      | 0.6627      | 23.0513     | 7.0010      | 0.2631 | 0.8651 | 0.8000 | 64.9548 |
| 0.8000                          | 1.8456      | 0.5466      | 0.6695      | 23.0458     | 7.0386      | 0.2196 | 0.8621 | 0.8000 | 64.9628 |
| 0.9000                          | 1.8298      | 0.5538      | 0.6752      | 23.0411     | 7.0786      | 0.1834 | 0.8591 | 0.8000 | 64.9696 |
| 1.0000                          | 1.8164      | 0.5599      | 0.6800      | 23.0370     | 7.1123      | 0.1534 | 0.8561 | 0.8000 | 64.9753 |
| 1.1000                          | 1.8052      | 0.5652      | 0.6839      | 23.0336     | 7.1408      | 0.1285 | 0.8531 | 0.8000 | 64.9802 |
| 1.2000                          | 1.7956      | 0.5696      | 0.6872      | 23.0306     | 7.1650      | 0.1078 | 0.8501 | 0.8000 | 64.9844 |
| 1.3000                          | 1.7875      | 0.5735      | 0.6900      | 23.0281     | 7.1856      | 0.0906 | 0.8471 | 0.8000 | 64.9879 |
| 1.4000                          | 1.7806      | 0.5767      | 0.6923      | 23.0259     | 7.2032      | 0.0763 | 0.8442 | 0.8000 | 64.9910 |
| 1.5000                          | 1.7746      | 0.5795      | 0.6942      | 23.0241     | 7.2184      | 0.0644 | 0.8413 | 0.8000 | 64.9937 |
| 1.6000                          | 1.7694      | 0.5820      | 0.6958      | 23.0225     | 7.2315      | 0.0545 | 0.8384 | 0.8000 | 64.9961 |
| 1.7000                          | 1.7650      | 0.5841      | 0.6971      | 23.0212     | 7.2429      | 0.0462 | 0.8355 | 0.8000 | 64.9982 |
| 1.8000                          | 1.7610      | 0.5859      | 0.6983      | 23.0200     | 7.2529      | 0.0394 | 0.8326 | 0.8000 | 65.0000 |
| 1.9000                          | 1.7576      | 0.5875      | 0.6993      | 23.0190     | 7.2617      | 0.0336 | 0.8298 | 0.8000 | 65.0017 |
| 2.0000                          | 1.7545      | 0.5890      | 0.7001      | 23.0181     | 7.2695      | 0.0289 | 0.8269 | 0.8000 | 65.0032 |
| 2.1000                          | 1.7518      | 0.5902      | 0.7008      | 23.0173     | 7.2764      | 0.0249 | 0.8241 | 0.8000 | 65.0045 |
| 2.2000                          | 1.7493      | 0.5914      | 0.7014      | 23.0166     | 7.2827      | 0.0216 | 0.8212 | 0.8000 | 65.0058 |
| 2.3000                          | 1.7471      | 0.5924      | 0.7019      | 23.0160     | 7.2884      | 0.0189 | 0.8184 | 0.8000 | 65.0069 |
| 2.4000                          | 1.7450      | 0.5933      | 0.7023      | 23.0155     | 7.2936      | 0.0166 | 0.8156 | 0.8000 | 65.0080 |
| 2.5000                          | 1.7431      | 0.5942      | 0.7027      | 23.0150     | 7.2985      | 0.0147 | 0.8128 | 0.8000 | 65.0090 |
| 2.6000                          | 1.7413      | 0.5950      | 0.7031      | 23.0146     | 7.3030      | 0.0131 | 0.8101 | 0.8000 | 65.0100 |
| 2.7000                          | 1.7396      | 0.5957      | 0.7034      | 23.0142     | 7.3072      | 0.0118 | 0.8073 | 0.8000 | 65.0109 |
| 2.8000                          | 1.7381      | 0.5964      | 0.7036      | 23.0138     | 7.3111      | 0.0106 | 0.8045 | 0.8000 | 65.0118 |
| 2.9000                          | 1.7366      | 0.5971      | 0.7039      | 23.0135     | 7.3149      | 0.0097 | 0.8018 | 0.8000 | 65.0126 |
| 3.0000                          | 1.7351      | 0.5977      | 0.7041      | 23.0131     | 7.3185      | 0.0089 | 0.7991 | 0.8000 | 65.0134 |
| 3.1000                          | 1.7338      | 0.5983      | 0.7043      | 23.0128     | 7.3220      | 0.0083 | 0.7963 | 0.8000 | 65.0142 |
| 3.2000                          | 1.7324      | 0.5988      | 0.7044      | 23.0125     | 7.3253      | 0.0078 | 0.7936 | 0.8000 | 65.0150 |
| TOL. ON EQUIL. CONSTANT NOT MET |             |             |             |             |             |        |        |        |         |
| 0.17866E-24                     | 0.25532E 15 | 0.21649E 03 | 0.65435E 12 | 0.27234E 13 | 0.22099E 21 |        |        |        |         |
| 0.17823E-24                     | 0.25563E 15 | 0.21020E 03 | 0.61762E 12 | 0.27233E 13 | 0.22098E 21 |        |        |        |         |



TEMP. 0.7000E 03 DEG. F 0.34198E 15  
 EQUIL. K 0.47915E 03 0.44823E 03 0.96269E 08 0.30000E 03  
 FORWARD K 0.82000E 05 0.11000E 04 0.10000E 05 0.23450E 06  
 BACKWARD K 0.42089E 05 0.24540E 01 0.11451E 02 0.23450E 06

| ***TIME*** | S02    | H2S    | SR     | H2O     | CU2    | CUS    | CU     | H2     | INERT   |
|------------|--------|--------|--------|---------|--------|--------|--------|--------|---------|
| EQUIL.     | 1.6032 | 2.7570 | 0.4002 | 21.5153 | 8.2711 | 0.0023 | 0.0000 | 0.0013 | 65.4491 |
| 0.0000     | 3.2300 | 3.1700 | 0.0000 | 20.0000 | 6.1200 | 1.0700 | 0.9500 | 0.0000 | 64.6300 |
| 0.1000     | 2.2606 | 1.7794 | 0.3683 | 21.5344 | 6.7266 | 0.5292 | 0.9648 | 0.0000 | 65.0313 |
| 0.2000     | 2.1992 | 1.9323 | 0.3894 | 21.3911 | 7.0061 | 0.2720 | 0.9459 | 0.0000 | 65.0382 |
| 0.3000     | 2.1662 | 2.0127 | 0.3998 | 21.3162 | 7.1547 | 0.1436 | 0.9276 | 0.0000 | 65.0733 |
| 0.4000     | 2.1468 | 2.0564 | 0.4050 | 21.2758 | 7.2381 | 0.0786 | 0.9098 | 0.0000 | 65.0828 |
| 0.5000     | 2.1341 | 2.0816 | 0.4077 | 21.2531 | 7.2902 | 0.0453 | 0.8924 | 0.0000 | 65.0895 |
| 0.6000     | 2.1249 | 2.0972 | 0.4091 | 21.2393 | 7.3249 | 0.0282 | 0.8755 | 0.0000 | 65.0947 |
| 0.7000     | 2.1176 | 2.1079 | 0.4099 | 21.2302 | 7.3509 | 0.0194 | 0.8588 | 0.0000 | 65.0971 |

| ***TIME*** | SO2    | H2S    | SB     | H2O     | CU2    | CUS    | CU     | M2     | INERT   |
|------------|--------|--------|--------|---------|--------|--------|--------|--------|---------|
| EQUIL.     | 1.8688 | 2.6106 | 0.4117 | 21.8685 | 7.3887 | 0.0019 | 0.0000 | 0.0012 | 62.8482 |
| 0.0000     | 3.4800 | 3.3800 | 0.0000 | 20.0000 | 5.6300 | 0.8200 | 0.8500 | 0.8000 | 62.0400 |
| 0.2500     | 2.4109 | 1.9535 | 0.4039 | 21.5875 | 6.4050 | 0.1366 | 0.8086 | 0.8086 | 62.4481 |
| 0.5000     | 2.3736 | 2.0271 | 0.4130 | 21.5207 | 6.5559 | 0.0302 | 0.7662 | 0.5071 | 62.5071 |
| 0.7500     | 2.3562 | 2.0497 | 0.4147 | 21.5019 | 6.6148 | 0.0123 | 0.7263 | 0.3177 | 62.5177 |
| 1.0000     | 2.3427 | 2.0633 | 0.4152 | 21.4915 | 6.6566 | 0.0090 | 0.6888 | 0.2564 | 62.5264 |
| 1.2500     | 2.3305 | 2.0749 | 0.4155 | 21.4828 | 6.6939 | 0.0082 | 0.6533 | 0.2345 | 62.5345 |
| 1.5000     | 2.3190 | 2.0857 | 0.4158 | 21.4747 | 6.7286 | 0.0078 | 0.6198 | 0.2120 | 62.5420 |
| 1.7500     | 2.3082 | 2.0958 | 0.4160 | 21.4671 | 6.7613 | 0.0074 | 0.5882 | 0.1911 | 62.5491 |
| 2.0000     | 2.2981 | 2.1055 | 0.4162 | 21.4599 | 6.7923 | 0.0071 | 0.5583 | 0.1723 | 62.5559 |
| 2.2500     | 2.2885 | 2.1146 | 0.4164 | 21.4530 | 6.8215 | 0.0069 | 0.5301 | 0.1562 | 62.5622 |

TEMP. 0.70000E 03 DEG. F 0.44823E 03 0.96269E 08 0.34196E 15  
 EQUIL. K 0.47915E 03 0.11000E 04 0.10000E 05 0.30000E 05  
 FORWARD K 0.82000E 05 0.11000E 04 0.11451E 02 0.23480E 06  
 BACKWARD K 0.42089E 05 0.24540E 01 0.11451E 02 0.23480E 06

| ***TIME*** | S02    | H2S    | S8     | H2O     | C02    | C0S    | C0     | m2     | inlet   |
|------------|--------|--------|--------|---------|--------|--------|--------|--------|---------|
| EQUIL.     | 1.6032 | 2.7570 | 0.4002 | 21.5153 | 8.2711 | 0.0023 | 0.0000 | 0.0013 | 02.4471 |
| 0.0000     | 3.2300 | 3.1700 | 0.0000 | 20.0000 | 6.1200 | 1.0700 | 0.9800 | 0.5000 | 02.5000 |
| 0.1000     | 2.2606 | 1.7794 | 0.3683 | 21.5344 | 6.7266 | 0.5292 | 0.9648 | 0.5000 | 02.5000 |
| 0.2000     | 2.1992 | 1.9323 | 0.3894 | 21.3911 | 7.0061 | 0.2720 | 0.9459 | 0.5000 | 02.5000 |
| 0.3000     | 2.1662 | 2.0127 | 0.3998 | 21.3162 | 7.1547 | 0.1436 | 0.9276 | 0.5000 | 02.5000 |
| 0.4000     | 2.1468 | 2.0564 | 0.4050 | 21.2758 | 7.2387 | 0.0786 | 0.9098 | 0.5000 | 02.5000 |
| 0.5000     | 2.1341 | 2.0816 | 0.4077 | 21.2531 | 7.2902 | 0.0433 | 0.8924 | 0.5000 | 02.5000 |
| 0.6000     | 2.1249 | 2.0972 | 0.4091 | 21.2393 | 7.3249 | 0.0282 | 0.8752 | 0.5000 | 02.5000 |
| 0.7000     | 2.1176 | 2.1079 | 0.4099 | 21.2302 | 7.3509 | 0.0194 | 0.8588 | 0.5000 | 02.5000 |
| 0.8000     | 2.1112 | 2.1160 | 0.4103 | 21.2235 | 7.3723 | 0.0147 | 0.8426 | 0.5000 | 02.5000 |
| 0.9000     | 2.1054 | 2.1227 | 0.4105 | 21.2182 | 7.3912 | 0.0123 | 0.8267 | 0.5000 | 02.5000 |
| 1.0000     | 2.1000 | 2.1286 | 0.4107 | 21.2135 | 7.4085 | 0.0109 | 0.8111 | 0.5000 | 02.5000 |
| 1.1000     | 2.0947 | 2.1341 | 0.4108 | 21.2092 | 7.4250 | 0.0102 | 0.7959 | 0.5000 | 02.5000 |
| 1.2000     | 2.0897 | 2.1393 | 0.4109 | 21.2052 | 7.4408 | 0.0094 | 0.7810 | 0.5000 | 02.5000 |
| 1.3000     | 2.0848 | 2.1444 | 0.4110 | 21.1976 | 7.4561 | 0.0092 | 0.7663 | 0.5000 | 02.5000 |
| 1.4000     | 2.0800 | 2.1493 | 0.4111 | 21.1939 | 7.4710 | 0.0090 | 0.7520 | 0.5000 | 02.5000 |
| 1.5000     | 2.0753 | 2.1540 | 0.4111 | 21.1903 | 7.4856 | 0.0088 | 0.7380 | 0.5000 | 02.5000 |
| 1.6000     | 2.0708 | 2.1587 | 0.4111 | 21.1868 | 7.4998 | 0.0087 | 0.7243 | 0.5000 | 02.5000 |
| 1.7000     | 2.0663 | 2.1633 | 0.4112 | 21.1833 | 7.5138 | 0.0086 | 0.7109 | 0.5000 | 02.5000 |
| 1.8000     | 2.0619 | 2.1678 | 0.4112 | 21.1799 | 7.5274 | 0.0085 | 0.6977 | 0.5000 | 02.5000 |
| 1.9000     | 2.0576 | 2.1722 | 0.4113 | 21.1766 | 7.5408 | 0.0084 | 0.6849 | 0.5000 | 02.5000 |
| 2.0000     | 2.0534 | 2.1765 | 0.4113 | 21.1734 | 7.5539 | 0.0083 | 0.6722 | 0.5000 | 02.5000 |
| 2.1000     | 2.0493 | 2.1807 | 0.4114 | 21.1702 | 7.5667 | 0.0082 | 0.6599 | 0.5000 | 02.5000 |
| 2.2000     | 2.0453 | 2.1849 | 0.4114 | 21.1670 | 7.5793 | 0.0081 | 0.6477 | 0.5000 | 02.5000 |
| 2.3000     | 2.0414 | 2.1890 | 0.4114 | 21.1639 | 7.5916 | 0.0080 | 0.6359 | 0.5000 | 02.5000 |
| 2.4000     | 2.0375 | 2.1930 | 0.4115 | 21.1609 | 7.6037 | 0.0078 | 0.6242 | 0.5000 | 02.5000 |
| 2.5000     | 2.0338 | 2.1969 | 0.4115 | 21.1579 | 7.6155 | 0.0077 | 0.6128 | 0.5000 | 02.5000 |
| 2.6000     | 2.0301 | 2.2007 | 0.4115 | 21.1550 | 7.6271 | 0.0076 | 0.6017 | 0.5000 | 02.5000 |
| 2.7000     | 2.0265 | 2.2045 | 0.4115 | 21.1521 | 7.6385 | 0.0075 | 0.5907 | 0.5000 | 02.5000 |
| 2.8000     | 2.0229 | 2.2082 | 0.4115 | 21.1493 | 7.6496 | 0.0074 | 0.5800 | 0.5000 | 02.5000 |
| 2.9000     | 2.0195 | 2.2119 | 0.4116 | 21.1466 | 7.6605 | 0.0073 | 0.5692 | 0.5000 | 02.5000 |
| 3.0000     | 2.0161 | 2.2154 | 0.4116 | 21.1438 | 7.6712 | 0.0072 | 0.5591 | 0.5000 | 02.5000 |
| 3.1000     | 2.0127 | 2.2189 | 0.4116 | 21.1438 | 7.6817 | 0.0071 | 0.5490 | 0.5000 | 02.5000 |

2. INTERMEDIATE REACTOR STUDIES

2. INTERMEDIATE REACTOR STUDIES



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## 2.1 INTRODUCTION

2.1.1 In the high temperature reduction of  $\text{SO}_2$  with methane, there are considerable concentrations of by-products formed in the primary reactor. Along with some unreacted  $\text{SO}_2$ ,  $\text{S}_x$ , and  $\text{H}_2\text{S}$ , there are present  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{COS}$  and  $\text{CS}_2$  constituents which represent yield losses and except for  $\text{COS}$ , remain unreacted in the subsequent Claus operation. Since high temperature primary reactor products normally contain negligible  $\text{CS}_2$  concentration, only  $\text{COS}$ ,  $\text{CO}$  and  $\text{H}_2$  were considered for investigation.

2.1.2 Without a reactor -- intermediate between the primary methane reductor and the Claus units -- that could react out these by-products with  $\text{SO}_2$ , reductant efficiency and sulfur yield would suffer. The function of the intermediate catalytic reactor or converter therefore, is to insure that sulfur,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and inerts are the only species entering the Claus units. This report summarizes the work performed aimed at optimizing the intermediate reactor conditions of temperature and contact time (or space velocity) while attempting to effect maximum conversion or reduction of  $\text{COS}$ ,  $\text{CO}$  and  $\text{H}_2$  to minimal concentrations.

## 2.2 SUMMARY

2.2.1 A laboratory investigation was conducted to establish the optimum temperature and contact time for the intermediate reactor. The study was subdivided into two phases: (a) investigation of variable contact time from 1/4-4 seconds using a fixed temperature of  $500^\circ\text{C}$  ( $932^\circ\text{F}$ ); and (b) study of various temperatures from  $350$ - $600^\circ\text{C}$  ( $662$ - $1112^\circ\text{F}$ ) using the optimum range of contact time obtained. These experimental parameters were correlated accordingly thereafter based on the conversion or consumption of  $\text{COS}$ ,  $\text{CO}$  and  $\text{H}_2$  components. Contact times used in this report are obtained by using a 50% voidage for the catalyst used.

2.2.2 Parameters fixed in the study were feed composition and type of catalyst. The intermediate reactor feed used was made of a synthetic gas mixture simulating a typical product of a high temperature primary  $\text{SO}_2$ /methane reactor. Porocel LPD was used as catalyst contained in a tubular Vycor glass reactor.

2.2.3 Complementary computer-based equilibrium calculations were conducted for the nominal feed to verify the actual experimental results.

## 2.3 CONCLUSIONS AND RECOMMENDATIONS

2.3.1 Initial conclusion derived from the first phase of the study indicated that at 932°F, contact times of about 1/2 second for COS, 1 second for CO and 5 seconds for H<sub>2</sub> were sufficient to reduce these gases to minimum concentrations. The optimum contact time range obtained was 1.0 ± 0.5 second.

2.3.2 At 1112°F and 1 second contact time, COS, CO and H<sub>2</sub> were essentially reacted out. The general trend insofar as the intermediate reactor conditions of temperature and contact time are concerned is that optimum conversion was favored at higher temperatures and shorter contact times or lower temperatures and longer contact times.

2.3.3 Each individual component in question exhibited its own preferred optimum temperature and contact time. Of the three, H<sub>2</sub> was the most difficult to react out followed by CO, then COS. H<sub>2</sub> was completely consumed at 1112°F and 1 second or at 1022°F and 3/2 seconds. CO was removed at 1058°F and 1/2 second or at 1022°F and 1 second. COS required 752°F and 1 second or 662°F and 3/2 seconds.

2.3.4 Results of this study, and in collaboration with data gathered from the overall reaction runs of the parallel normal temperature Claus (NTC) studies conducted at relatively lower temperature range of about 400-700°F, indicated a necessity for an intermediate reactor. With the three subject by-products combined, only COS reacted out favorably in the NTC 700°F overall reaction runs and confirmed by our 662°F and 752°F runs. CO and H<sub>2</sub> needed temperatures higher than the NTC temperature range to be completely reacted.

2.3.5 Comparison between experimental results and computer generated equilibrium compositions indicated very close agreement as the experimental conditions approached the optimum.

## 2.4 EXPERIMENTATION AND DISCUSSION

### 2.4.1 Apparatus

An existing test stand or apparatus was modified to conform with the requirements of the intermediate reactor studies. An illustrative diagram of the equipment set-up is shown in Exhibit No. 2-15. The set-up was composed mainly of a gas feed manifold or flowmeters control panel, nitrogen H<sub>2</sub>O saturator, tubular glass reactor enclosed in a three-zone vertically mounted furnace and stack. Exhibit No. 2-16 is a diagram of the sampling system used for both the feed and exit gases.



## 2.4.2 Catalyst

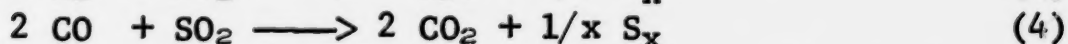
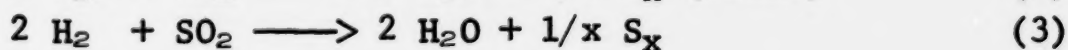
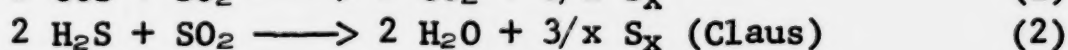
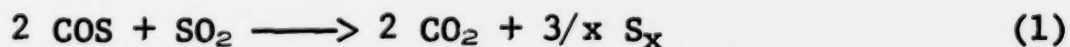
The catalyst used in this study was 1/4" x 3/8" Porocel LPD. The material was supplied by Porocel Corporation of Little Rock, Arkansas. A 10-inch high catalyst bed was used and charged into a 2-inch diameter tubular Vycor glass reactor. After every week of usage during the experimentation, the spent catalyst is replaced with fresh batch in order to insure uniformity of results. A 50% voidage figure was used in calculating the actual contact times used in this report.

## 2.4.3 Theoretical Feed Composition

2.4.3.1 As aforementioned, the intermediate reactor feed composition used was typical of a high temperature SO<sub>2</sub>/methane reduction product. The first feed composition proposed for this study was to contain, volumewise: 2.5% SO<sub>2</sub>, 2.0% H<sub>2</sub>S, 1.0% COS, 1.0% CO, 1.0% H<sub>2</sub>, 5.0% CO<sub>2</sub>, 11.0% H<sub>2</sub>O and 76.5% N<sub>2</sub>. COS, CO and H<sub>2</sub> were fixed at 1.0% each in order to have a common basis for later comparison of performance. However, one important component absent in the above composition was sulfur. Since it was obviously difficult to meter sulfur as it is, concentrations of H<sub>2</sub>S and SO<sub>2</sub> were modified from 2.0% and 2.5% to 5.0% and 4.0%, respectively, the other components remain unchanged. The main reason for increasing H<sub>2</sub>S and SO<sub>2</sub> concentrations was to allow sufficient S<sub>x</sub> formation in the feed stream in order to better simulate the actual primary methane reductor product gas composition which contain S<sub>x</sub>. Another aim was to provide H<sub>2</sub>S and SO<sub>2</sub> concentrations in the intermediate reactor exit stream which are suitable for feed to the Claus converters.

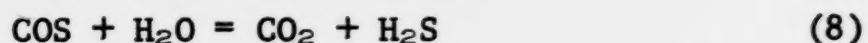
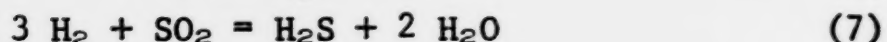
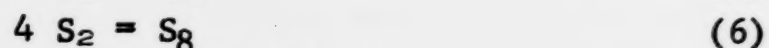
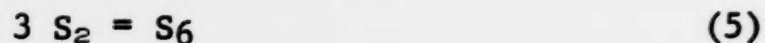
2.4.3.2 The modified feed composition is found in Exhibit No. 2-1. CS<sub>2</sub> and unreacted CH<sub>4</sub> components were not included in the feed composition because they occur in negligible concentrations in most high temperature SO<sub>2</sub>/CH<sub>4</sub> reduction processes.

2.4.3.3 The concentrations of the reacting constituents in the feed are balanced in proper stoichiometric proportions such that the following reactions prevail:



For every 2 moles each of COS, CO, H<sub>2</sub> and H<sub>2</sub>S there should be present one equivalent mole of oxidant SO<sub>2</sub>. Therefore, for the combined 8 moles of the reductants in the feed 4 moles of SO<sub>2</sub> would be needed.

2.4.3.4 Other reactions are also possible, some occurring to a very limited extent if at all:



#### 2.4.4 Laboratory Procedure

2.4.4.1 The laboratory procedure followed for completing a run consisted mainly of the following steps: (a) taking the temperature profile; (b) sampling; (c) GC analysis; and (d) evaluation of results.

2.4.4.2 Before a run was started, the whole system was first brought under steady state conditions by feeding into the reactor all the necessary gas flows through the flowmeters control panel (see Exhibit No. 2-15) and adjusting the heat input through the three-zone temperature controller until the catalyst bed temperature becomes constant. An isothermal condition was established by frequently checking the temperature profile of the catalyst bed along the 10-inch bed height at 2" intervals and the midpoint at the 5" level. A profile reading of the isothermal bed was recorded for every run made.

2.4.4.3 After taking the temperature profile, three feed and three exit samples for each run were then obtained for subsequent gas chromatographic analysis. Anhydrous  $CaCl_2$  was used as the drying agent to remove  $H_2S$  and elemental sulfur from the samples (see Exhibit No. 2-16).

2.4.4.4 In performing the analysis, the GC instrument was first run with 3 to 5 shots of dilute  $H_2S$  gas to condition the fractionating column, as this gas is the most troublesome to analyze. Actual samples were then analyzed after the instrument was conditioned. Analytical results were subsequently evaluated to correlate the pertinent parameters involved.

#### 2.4.5 Discussion of Results

2.4.5.1 Experimental conditions and analytical results of all runs are summarized in the exhibits that follow. Exit analysis is presented as "normalized" values as derived from actual chromatographic analysis. Due to the resulting volume decrease from removal of  $H_2O$  and  $S_x$  in the exit stream, all the remaining components increase correspondingly



thus bringing forth an inherent error in the actual GC analysis. Calculations for normalized exit values are based on maintaining a similar  $N_2$  concentration in both feed and exit streams, the other components being adjusted accordingly. This was done since  $N_2$  was the only component in the feed whose concentration did not change basically in the exit. All the others including  $H_2O$  and  $CO_2$  were subject to change.

2.4.5.2 Experimental data of the initial phase of investigation are shown in Exhibit No. 2-2. Normalized COS, CO and  $H_2$  exit concentrations are plotted against contact time at a constant temperature of  $932^\circ F$  in Exhibit No. 2-3 to show the rate of disappearance of said components relative to contact time. Percent conversions or consumptions of these components are tabulated in Exhibit No. 2-4 and Exhibit No. 2-5 plots these conversions versus contact time.

2.4.5.3 Initial phase results indicate that for optimum conversions of COS, CO and  $H_2$  at  $932^\circ F$ , it takes about  $1/2$  second for COS, about 1 second for CO and about 5 seconds for  $H_2$  to reach equilibrium concentrations.  $1.0 \pm 0.5$  second was the optimum contact range obtained.

2.4.5.4 The original plan for the final phase of study to test variable temperatures from  $662-1292^\circ F$  in  $90^\circ F$  intervals at contact times of  $1/2$ , 1 and  $3/2$  seconds was modified when results obtained at  $1112^\circ F$  indicated that higher temperature runs were not needed. Maximum conversion or reduction of COS, CO and  $H_2$  to minimal concentrations has been demonstrated at about  $1022-1112^\circ F$  as shown by the experimental data in Exhibit No. 2-6.

2.4.5.5 Computer-based equilibrium calculations for the theoretical feed are given in Exhibit No. 2-7 at temperatures of  $662-1112^\circ F$  in  $90^\circ F$  intervals. Actual experimental results are compatible with this data as temperatures are increased to bring contact times into practical ranges.

2.4.5.6 Percent conversions of COS, CO and  $H_2$  at the aforesaid ranges of pertinent parameters are are tabulated in Exhibit No. 2-8. Graphical correlation between percent conversion, contact time and temperature are plotted in Exhibit Nos. 2-9, 2-10, and 2-11 corresponding to contact times of  $1/2$ , 1 and  $3/2$  seconds, respectively.

2.4.5.7 From the computer calculated equilibrium compositions of Exhibit No. 2-7, COS, CO and  $H_2$  percent conversions were calculated and compared with actual experimental results in Exhibit No. 2-12.

Experimental conversion values were arbitrarily taken from the 3/2 second contact time results where the components in question had sufficient data that approached equilibrium conditions at some particular temperatures. The dotted lines in this exhibit which correspond to certain temperatures indicate that experimental values below these lines have attained equilibrium conditions at the indicated temperatures and above.

2.4.5.8 For COS, conversion trend is identical in both experimental and equilibrium values of Exhibit No. 2-12 although the quantities have very slight discrepancies. In CO, however, there is very close agreement. The discrepancy for H<sub>2</sub> is somewhat appreciable due to the fact that the very slight inaccuracy in GC analysis is magnified in the extremely low concentration range of H<sub>2</sub>. This occurred even with a highly sensitive GC such as the Perkin-Elmer 820 we used which contained a very responsive hot wire detector. Other types of GC with less sensitive thermal conductivity detectors can hardly identify H<sub>2</sub> at about 1.0 volume percent range and lower. Despite the above, however, the overall agreement is quite evident as the experimental data approached equilibrium conditions.

2.4.5.9 Exhibit No. 2-13 shows the conditions of temperature and contact time required to obtain 95% or better conversion for COS, CO and H<sub>2</sub>. If H<sub>2</sub> is present in substantial amount in the primary reactor product, the intermediate reactor conditions should be at 1112°F and 1 second contact time to completely consume this by-product. At such conditions, however, COS and CO have already been eliminated. It is apparent therefore, that higher temperature and longer contact time favor H<sub>2</sub> removal whereas it takes much lower temperatures and shorter contact times for both COS and CO to disappear. Hence, in a situation where either COS or CO is abundant in the primary reactor product and the other by-products are negligible the intermediate reactor could operate as low as 662°F or 932°F, as the case maybe.

2.4.5.10 For an isothermal catalyst bed, the tolerated variance in temperature during the experimentation was about ±9°F although in most cases fluctuation of about ±4°F was common. Typical temperature profiles of the 662-1112°F runs along the 10" catalyst bed height are shown in Exhibit No. 2-14.

## 2.5 REFERENCE

1. Fleming, E. P. and Fitt, T. C., "High Purity Sulfur from Smelter Gases - Reduction with Natural Gas", Industrial and Engineering Chemistry, Vol. 42, No. 11, November 1950, pp. 2249-2253.

EXHIBIT NO. 2-1

Intermediate Reactor  
Theoretical Feed Composition  
(Volume %)

| Component        | Wet Basis | Dry Basis |
|------------------|-----------|-----------|
| CO <sub>2</sub>  | 5.0       | 5.6       |
| COS              | 1.0       | 1.1       |
| H <sub>2</sub> S | 5.0       | 5.6       |
| CS <sub>2</sub>  | -         | -         |
| SO <sub>2</sub>  | 4.0       | 4.5       |
| H <sub>2</sub>   | 1.0       | 1.1       |
| O <sub>2</sub>   | -         | -         |
| N <sub>2</sub>   | 72.0      | 81.0      |
| CH <sub>4</sub>  | -         | -         |
| CO               | 1.0       | 1.1       |
| H <sub>2</sub> O | 11.0      | -         |
| Total            | 100.0     | 100.0     |



# EXHIBIT NO. 2-2

## Initial Phase Experimental Data

| Run No. | Contact Time, (Sec.) | Nominal Temp. (°F) | Gas Composition (Volume %) |                  |      |      |                |                             |                |                 |                  |      |      |                |                 |                |
|---------|----------------------|--------------------|----------------------------|------------------|------|------|----------------|-----------------------------|----------------|-----------------|------------------|------|------|----------------|-----------------|----------------|
|         |                      |                    | Feed (Dry Basis)           |                  |      |      |                | Exit (Dry and S-Free Basis) |                |                 |                  |      |      |                |                 |                |
|         |                      |                    | SO <sub>2</sub>            | H <sub>2</sub> S | CO   | COS  | H <sub>2</sub> | CO <sub>2</sub>             | N <sub>2</sub> | SO <sub>2</sub> | H <sub>2</sub> S | CO   | COS  | H <sub>2</sub> | CO <sub>2</sub> | N <sub>2</sub> |
| IR-3    | 0.345                | 932                | 3.78                       | 5.18             | 1.20 | 1.60 | 0.79           | 4.27                        | 83.17          | 1.64            | 3.10             | 0.47 | 0.04 | 0.53           | 6.25            | 83.17          |
| IR-1    | 0.69                 | 932                | 4.12                       | 4.57             | 1.14 | 1.01 | 0.80           | 6.01                        | 82.28          | 1.58            | 1.93             | 0.10 | 0.03 | 0.43           | 7.90            | 82.28          |
| IR-5    | 1.0                  | 932                | 3.51                       | 4.09             | 0.92 | 0.87 | 0.68           | 6.14                        | 83.73          | 1.33            | 2.27             | 0.03 | 0.03 | 0.29           | 7.68            | 83.73          |
| IR-2    | 1.38                 | 932                | 3.58                       | 4.57             | 1.43 | 0.81 | 0.83           | 5.88                        | 82.83          | 1.64            | 2.87             | 0.04 | 0.02 | 0.32           | 8.00            | 82.83          |
| IR-6    | 2.0                  | 932                | 4.14                       | 4.61             | 1.45 | 0.84 | 0.87           | 6.08                        | 81.90          | 2.01            | 3.68             | 0.01 | 0.02 | 0.20           | 8.95            | 81.90          |
| IR-4    | 2.76                 | 932                | 4.35                       | 5.60             | 1.55 | 0.75 | 0.90           | 5.68                        | 81.15          | 1.32            | 3.20             | 0.0  | 0.02 | 0.22           | 7.15            | 81.15          |
| IR-7    | 4.0                  | 932                | 5.22                       | 6.36             | 0.54 | 1.87 | 1.44           | 9.76                        | 74.79          | 1.11            | 4.40             | 0.01 | 0.06 | 0.14           | 10.42           | 74.79          |

Average Feed Concentrations: (Excluding IR-7)

CO = 1.28%  
COS = 0.98%  
H<sub>2</sub> = 0.81%



**EXHIBIT NO. 2-3**  
**COS, CO & H<sub>2</sub> Exit**  
**Concentrations vs. Contact**  
**Time Plots at 932°F**

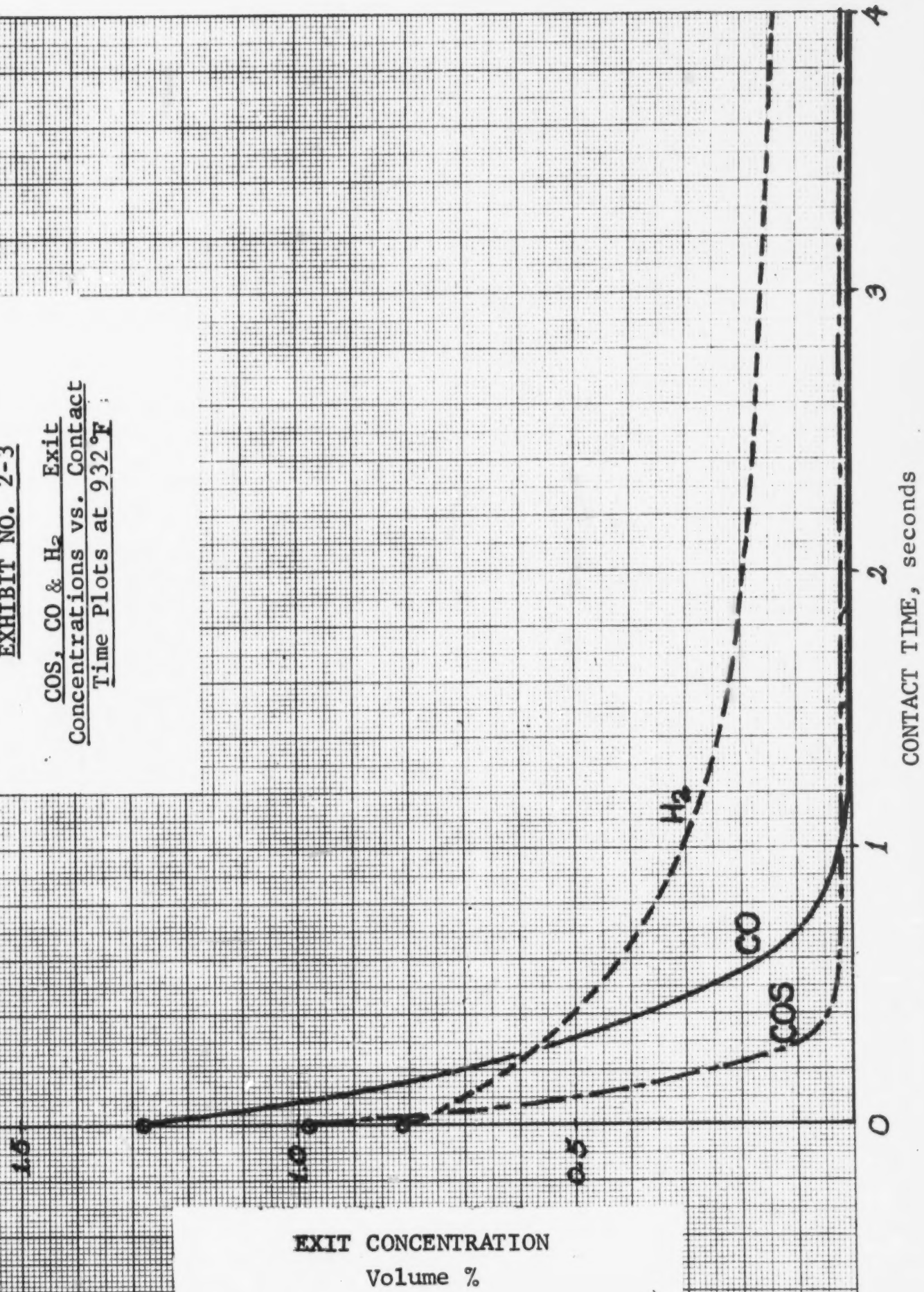


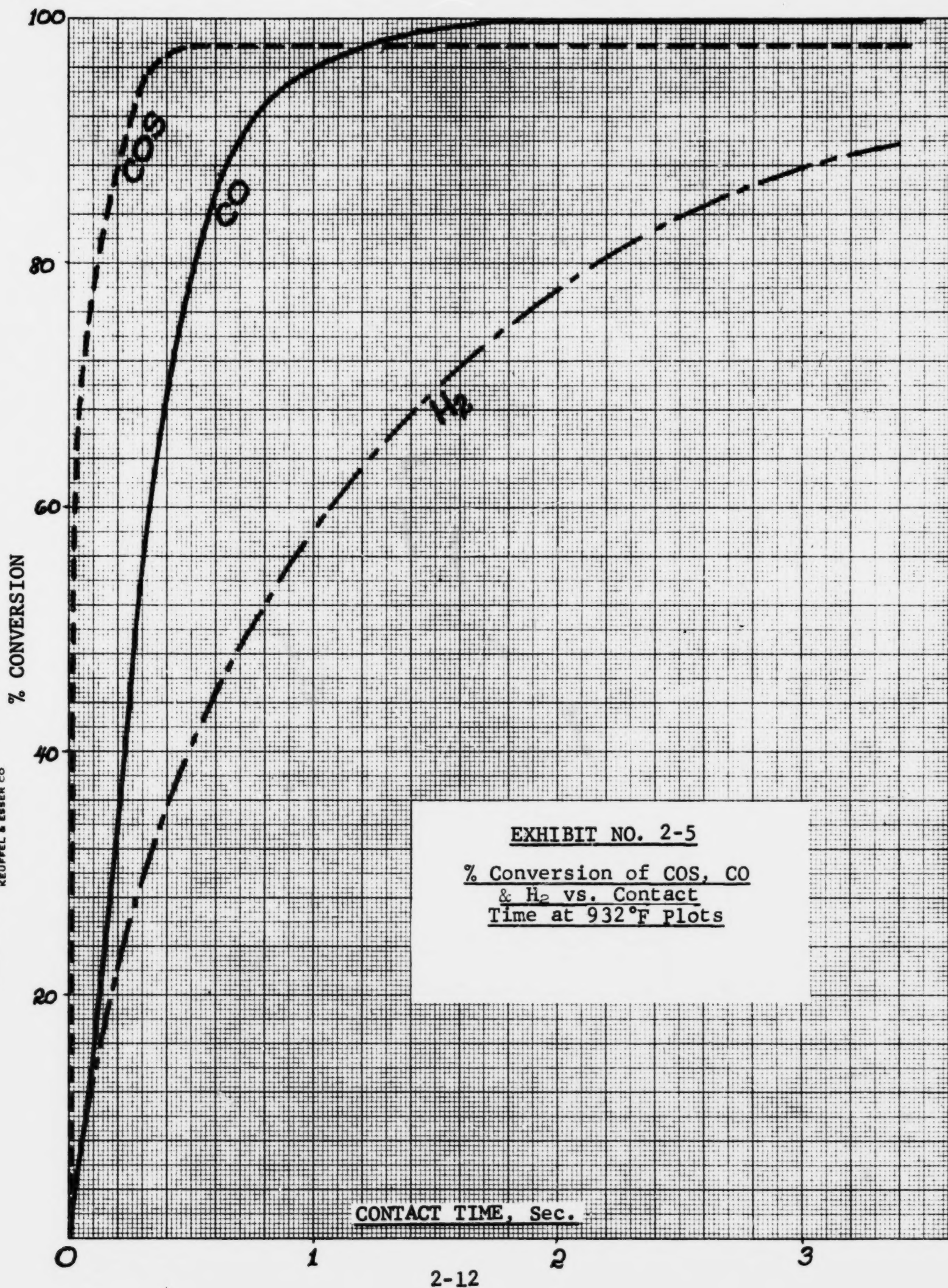
EXHIBIT NO. 2-4

Contact Time Optimization at 932°F  
Percent Conversion Table

| Run No. | Contact Time<br>Sec. | Nominal<br>Temp.<br>°F |      |       |                |
|---------|----------------------|------------------------|------|-------|----------------|
|         |                      |                        | COS  | CO    | H <sub>2</sub> |
| IR-3    | 0.345                | 932                    | 97.5 | 60.8  | 32.9           |
| IR-1    | 0.69                 | 932                    | 97.0 | 91.2  | 46.2           |
| IR-5    | 1.0                  | 932                    | 96.6 | 96.8  | 57.4           |
| IR-2    | 1.38                 | 932                    | 97.5 | 97.2  | 61.4           |
| IR-6    | 2.0                  | 932                    | 97.6 | 99.3  | 77.0           |
| IR-4    | 2.76                 | 932                    | 97.3 | 100.0 | 75.5           |
| IR-7    | 4.0                  | 932                    | 96.8 | 98.2  | 90.3           |



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# EXHIBIT NO. 2-6

## Final Phase Experimental Data

| Run No. | Nominal Temp. °F | Contact Time, Sec. | Gas Composition, Volume % |      |                |                  |                 |                                      |                |                 |                 |                |
|---------|------------------|--------------------|---------------------------|------|----------------|------------------|-----------------|--------------------------------------|----------------|-----------------|-----------------|----------------|
|         |                  |                    | Feed (Dry Basis)          |      |                |                  |                 | Normalized Exit (Dry & S-Free Basis) |                |                 |                 |                |
|         |                  |                    | CO <sub>2</sub>           | CO   | H <sub>2</sub> | H <sub>2</sub> S | SO <sub>2</sub> | CO <sub>2</sub>                      | N <sub>2</sub> | CO <sub>2</sub> | SO <sub>2</sub> | N <sub>2</sub> |
| IR-16   | 662              | 0.5                | 1.05                      | 1.41 | 0.88           | 5.47             | 4.69            | 5.70                                 | 80.77          | 0.42            | 1.28            | 0.84           |
| IR-15   | 662              | 1.0                | 1.19                      | 0.73 | 0.84           | 5.58             | 4.74            | 6.33                                 | 80.59          | 0.05            | 0.59            | 0.74           |
| IR-17   | 662              | 1.5                | 1.45                      | 0.73 | 0.71           | 5.59             | 4.88            | 5.91                                 | 80.69          | 0.01            | 0.58            | 0.60           |
| IR-10   | 752              | 0.5                | 1.22                      | 0.83 | 0.83           | 5.34             | 4.33            | 6.56                                 | 80.85          | 0.10            | 0.69            | 0.72           |
| IR-9    | 752              | 1.0                | 1.36                      | 0.71 | 0.73           | 5.22             | 3.95            | 6.97                                 | 80.86          | 0.01            | 0.42            | 0.48           |
| IR-11   | 752              | 1.5                | 1.21                      | 0.81 | 1.39           | 5.01             | 4.52            | 7.21                                 | 79.80          | 0.01            | 0.46            | 1.01           |
| IR-19   | 842              | 0.5                | 1.24                      | 0.67 | 0.90           | 5.19             | 4.35            | 5.95                                 | 81.71          | 0.03            | 0.48            | 0.69           |
| IR-18   | 842              | 1.5                | 1.25                      | 0.73 | 0.77           | 5.60             | 4.85            | 6.63                                 | 80.13          | 0.02            | 0.23            | 0.41           |
| IR-20   | 842              | 1.5                | 1.60                      | 0.84 | 1.06           | 5.86             | 4.71            | 6.88                                 | 79.0           | 0.03            | 0.09            | 0.55           |
| IR-24   | 932              | 0.5                | 1.38                      | 0.84 | 0.74           | 5.73             | 4.63            | 6.21                                 | 80.44          | 0.03            | 0.18            | 0.46           |
| IR-5    | 932              | 1.0                | 1.01                      | 1.14 | 0.80           | 4.09             | 3.51            | 6.14                                 | 83.73          | 0.03            | 0.03            | 0.29           |
| IR-25   | 932              | 1.5                | 1.38                      | 0.79 | 0.79           | 4.72             | 4.28            | 5.06                                 | 82.72          | 0.02            | 0.01            | 0.26           |
| IR-22   | 1022             | 0.5                | 1.55                      | 0.82 | 0.80           | 5.70             | 4.62            | 6.39                                 | 80.03          | 0.03            | 0.02            | 0.37           |
| IR-21   | 1022             | 1.0                | 1.25                      | 0.71 | 0.66           | 5.54             | 4.90            | 6.75                                 | 79.98          | 0.03            | 0               | 0.08           |
| IR-23   | 1022             | 1.5                | 1.30                      | 0.67 | 0.59           | 4.03             | 3.97            | 6.42                                 | 82.75          | 0.04            | 0               | 0              |
| IR-13   | 1112             | 0.5                | 1.39                      | 0.74 | 0.78           | 5.07             | 4.46            | 6.35                                 | 81.20          | 0.05            | 0               | 0.07           |
| IR-12   | 1112             | 1.0                | 1.30                      | 0.62 | 0.71           | 5.46             | 5.20            | 7.42                                 | 79.27          | 0.05            | 0               | 0              |
| IR-14   | 1112             | 1.5                | 1.73                      | 0.78 | 0.72           | 4.97             | 4.72            | 7.60                                 | 79.46          | 0.05            | 0               | 0              |



EXHIBIT NO. 2-7

Computer-Based Equilibrium Compositions

| Component        | Initial Moles | Equilibrium Moles |                |                |                |                 |                 |           |           |
|------------------|---------------|-------------------|----------------|----------------|----------------|-----------------|-----------------|-----------|-----------|
|                  |               | 660°F<br>349°C    | 759°F<br>404°C | 840°F<br>449°C | 939°F<br>504°C | 1020°F<br>549°C | 1119°F<br>604°C |           |           |
| CH <sub>4</sub>  | 0.0           | 0.00000           | 0.00000        | 0.00000        | 0.00000        | 0.00000         | 0.00000         | 0.00000   | 0.00000   |
| SO <sub>2</sub>  | 4.00000       | 1.00669           | 1.56003        | 1.96478        | 2.10146        | 1.99438         | 1.85474         | 1.85474   | 1.85474   |
| H <sub>2</sub> O | 11.00000      | 14.98829          | 13.88483       | 13.08012       | 12.81361       | 13.03315        | 13.32186        | 13.32186  | 13.32186  |
| H <sub>2</sub> S | 5.00000       | 2.01103           | 3.11313        | 3.91555        | 4.17620        | 3.94785         | 3.64010         | 3.64010   | 3.64010   |
| CO <sub>2</sub>  | 5.00000       | 6.99832           | 6.99510        | 6.99032        | 6.98347        | 6.97810         | 6.96868         | 6.96868   | 6.96868   |
| CO               | 1.00000       | 0.00001           | 0.00009        | 0.00030        | 0.00111        | 0.00278         | 0.00761         | 0.00761   | 0.00761   |
| S <sub>2</sub>   | 0.0           | 0.09391           | 0.41755        | 1.02090        | 1.75615        | 2.00983         | 2.23986         | 2.23986   | 2.23986   |
| H <sub>2</sub>   | 1.00000       | 0.00068           | 0.00204        | 0.00433        | 0.01019        | 0.01901         | 0.03805         | 0.03805   | 0.03805   |
| COS              | 1.00000       | 0.00166           | 0.00481        | 0.00938        | 0.01541        | 0.01911         | 0.02370         | 0.02370   | 0.02370   |
| CS <sub>2</sub>  | 0.0           | 0.00000           | 0.00000        | 0.00000        | 0.00001        | 0.00001         | 0.00002         | 0.00002   | 0.00002   |
| S <sub>6</sub>   | 0.0           | 0.04257           | 0.05749        | 0.04762        | 0.01081        | 0.00185         | 0.00023         | 0.00023   | 0.00023   |
| S <sub>8</sub>   | 0.0           | 0.81717           | 0.51775        | 0.22285        | 0.01622        | 0.00098         | 0.00004         | 0.00004   | 0.00004   |
| N <sub>2</sub>   | 72.00000      | 72.00000          | 72.00000       | 72.00000       | 72.00000       | 72.00000        | 72.00000        | 72.00000  | 72.00000  |
| Total            | 100.00000     | 97.96034          | 98.55282       | 99.25615       | 99.88465       | 100.00705       | 100.09487       | 100.09487 | 100.09487 |

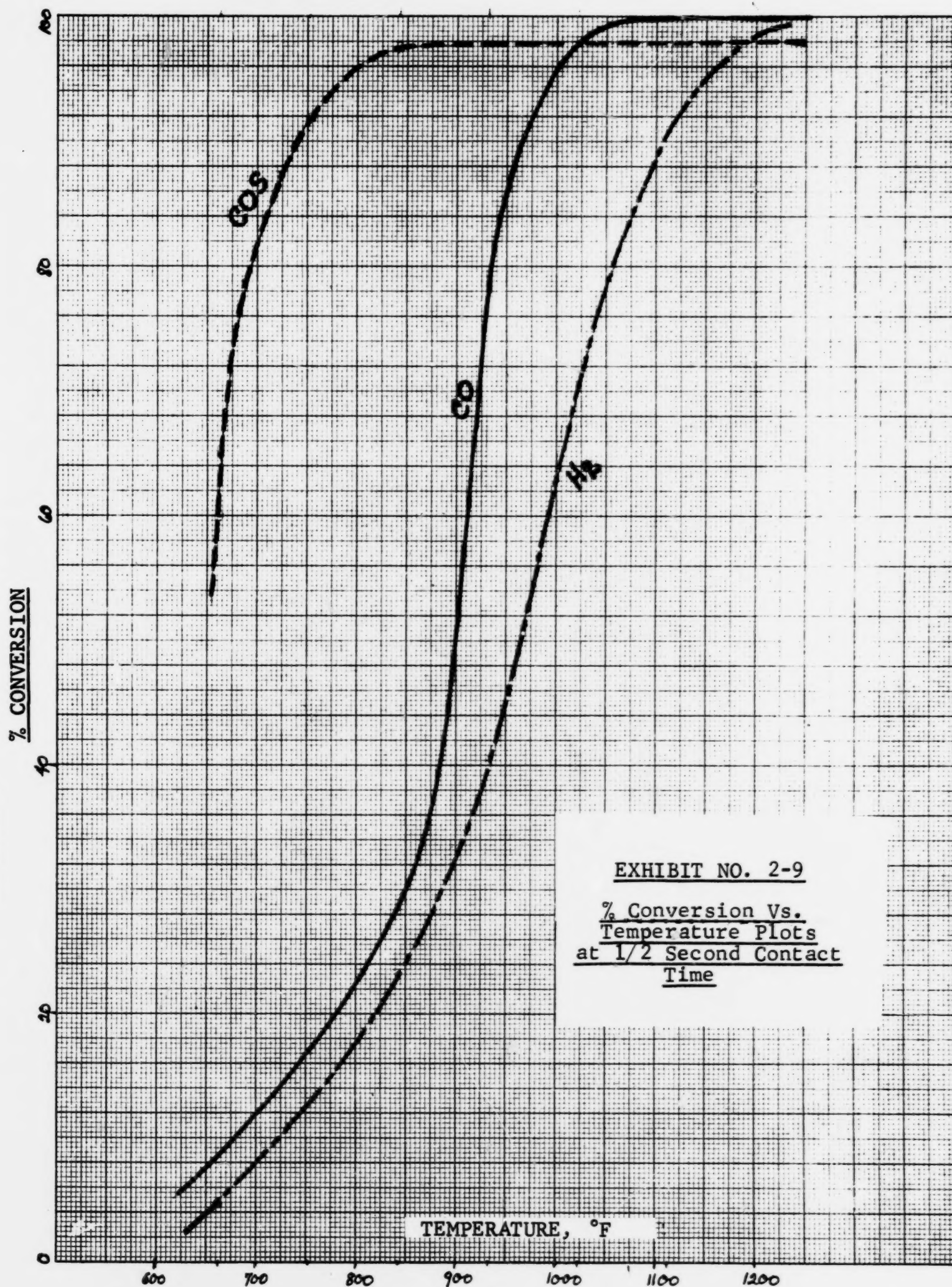


EXHIBIT NO. 2-8

Conversion Table for COS, CO and H<sub>2</sub>

| Nominal<br>Temp., °F | Component      | Contact Time, Sec. |       |        |
|----------------------|----------------|--------------------|-------|--------|
|                      |                | 1/2                | 1     | 3/2    |
| 662                  | COS            | 60.0%              | 95.8% | 99.3%  |
| 662                  | CO             | 9.2%               | 19.2% | 20.6%  |
| 662                  | H <sub>2</sub> | 4.6%               | 11.9% | 15.5%  |
| 752                  | COS            | 91.8%              | 99.2% | 99.2%  |
| 752                  | CO             | 16.9%              | 40.8% | 43.2%  |
| 752                  | H <sub>2</sub> | 13.3%              | 34.2% | 27.4%  |
| 842                  | COS            | 97.6%              | 98.3% | 98.2%  |
| 842                  | CO             | 27.9%              | 68.5% | 89.2%  |
| 842                  | H <sub>2</sub> | 23.3%              | 46.8% | 48.0%  |
| 932                  | COS            | 97.7%*             | 96.6% | 97.5%* |
| 932                  | CO             | 78.0%*             | 96.8% | 99.0%* |
| 932                  | H <sub>2</sub> | 40.0%*             | 57.4% | 70.0%* |
| 1022                 | COS            | 98.1%              | 97.6% | 96.9%  |
| 1022                 | CO             | 97.6%              | 100 % | 100 %  |
| 1022                 | H <sub>2</sub> | 53.8%              | 87.9% | 100 %  |
| 1112                 | COS            | 96.4%              | 96.2% | 97.1%  |
| 1112                 | CO             | 100 %              | 100 % | 100 %  |
| 1112                 | H <sub>2</sub> | 91.0%              | 100 % | 100 %  |

\* Interpolated values from Exhibit No. 2-5 of initial phase study. Analytical results of confirmatory runs for these interpolated values are shown in Exhibit No. 6.





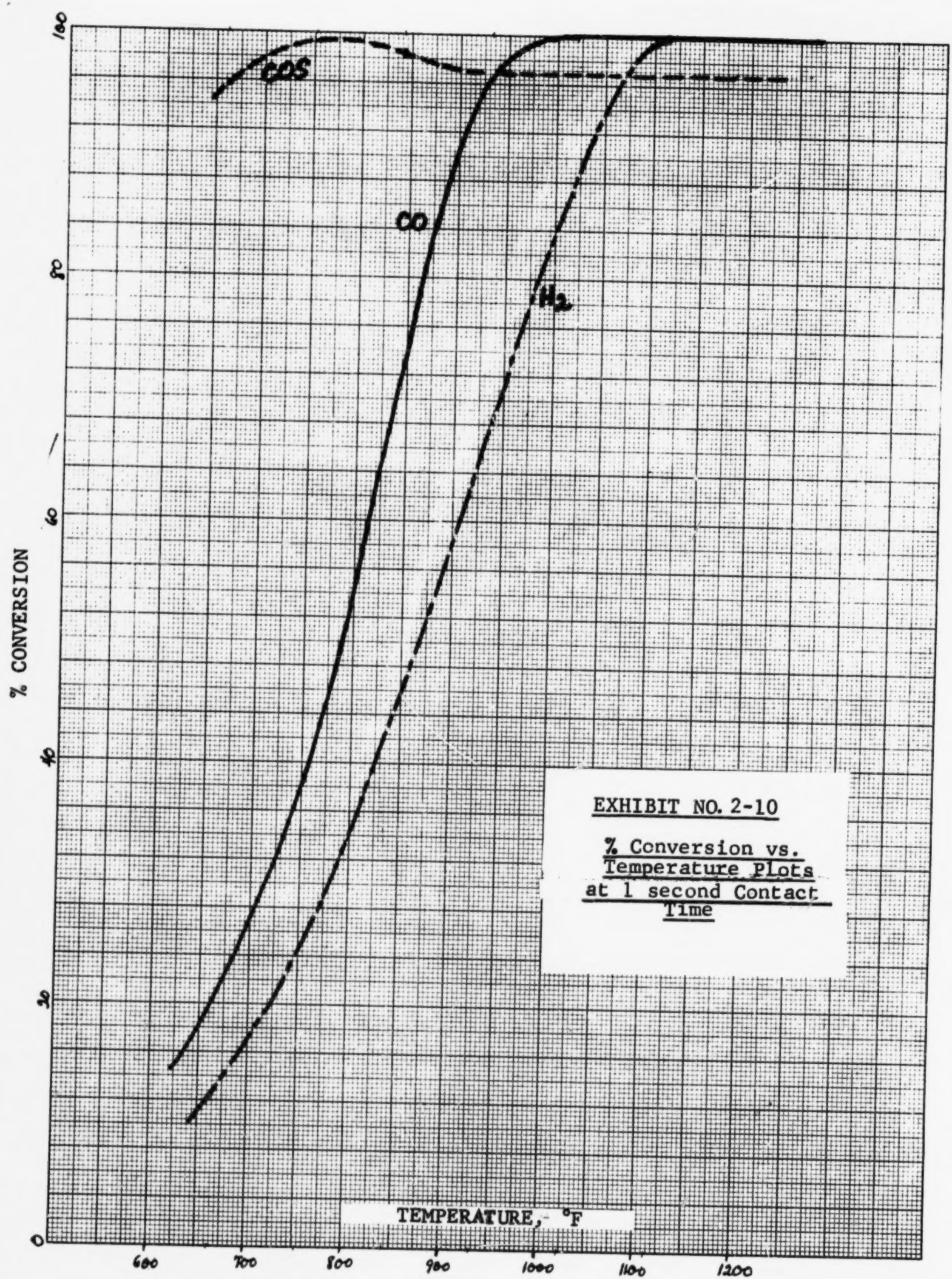


EXHIBIT NO. 2-10  
% Conversion vs.  
Temperature Plots  
at 1 second Contact  
Time

11 TO 12  
18 x 25 CM  
K<sup>o</sup>E  
KEUFFEL & ESSER CO.

% CONVERSION

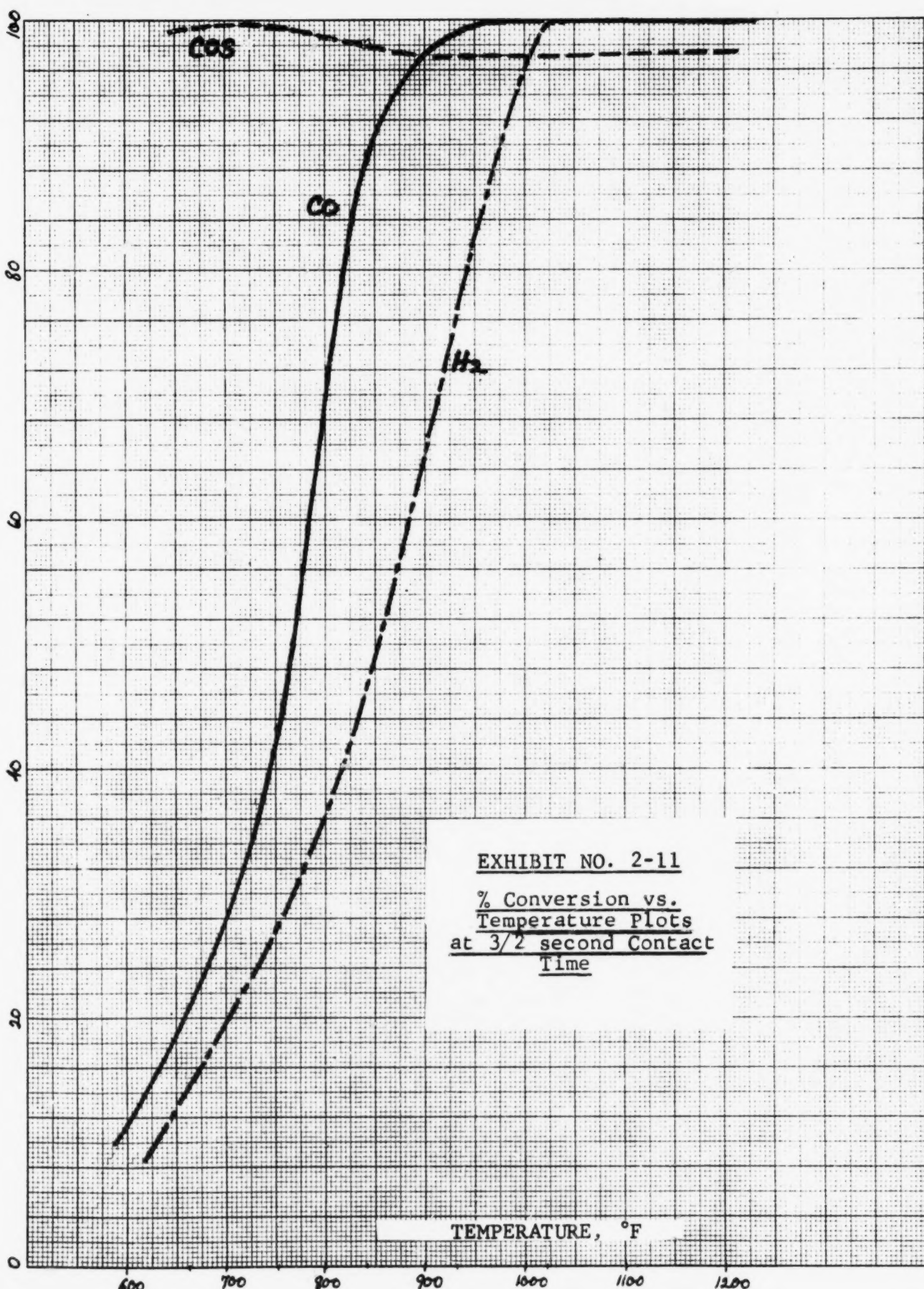


EXHIBIT NO. 2-11  
% Conversion vs.  
Temperature Plots  
at 3/2 second Contact  
Time

TEMPERATURE, °F



EXHIBIT NO. 2-12

Comparison of Percent Conversions Between Experimental Results\* and Computer Calculated Equilibrium Values

| Temp., °F | Percent Conversion   |                    |                      |                    |                      |                    |
|-----------|----------------------|--------------------|----------------------|--------------------|----------------------|--------------------|
|           | COS                  |                    | CO                   |                    | H <sub>2</sub>       |                    |
|           | Experimental Results | Equilibrium Values | Experimental Results | Equilibrium Values | Experimental Results | Equilibrium Values |
| 660       | 99.3                 | 99.8               | 20.6                 | 100                | 15.5                 | 99.9               |
| 759       | 99.2                 | 99.5               | 43.2                 | 100                | 27.4                 | 99.8               |
| 840       | 98.2                 | 99.1               | 89.2                 | 100                | 48.0                 | 99.6               |
| 939       | 97.5                 | 98.5               | 99.0                 | 99.9               | 70.0                 | 99.0               |
| 1020      | 96.9                 | 98.1               | ~ 100                | 99.7               | ~ 100                | 98.1               |
| 1119      | 97.1                 | 97.6               | ~ 100                | 99.2               | ~ 100                | 96.2               |

\* Experimental values were taken from 3/2 second contact time results.

EXHIBIT NO. 2-13

Optimum Conditions Required for  
>95% Conversion of COS, CO & H<sub>2</sub>

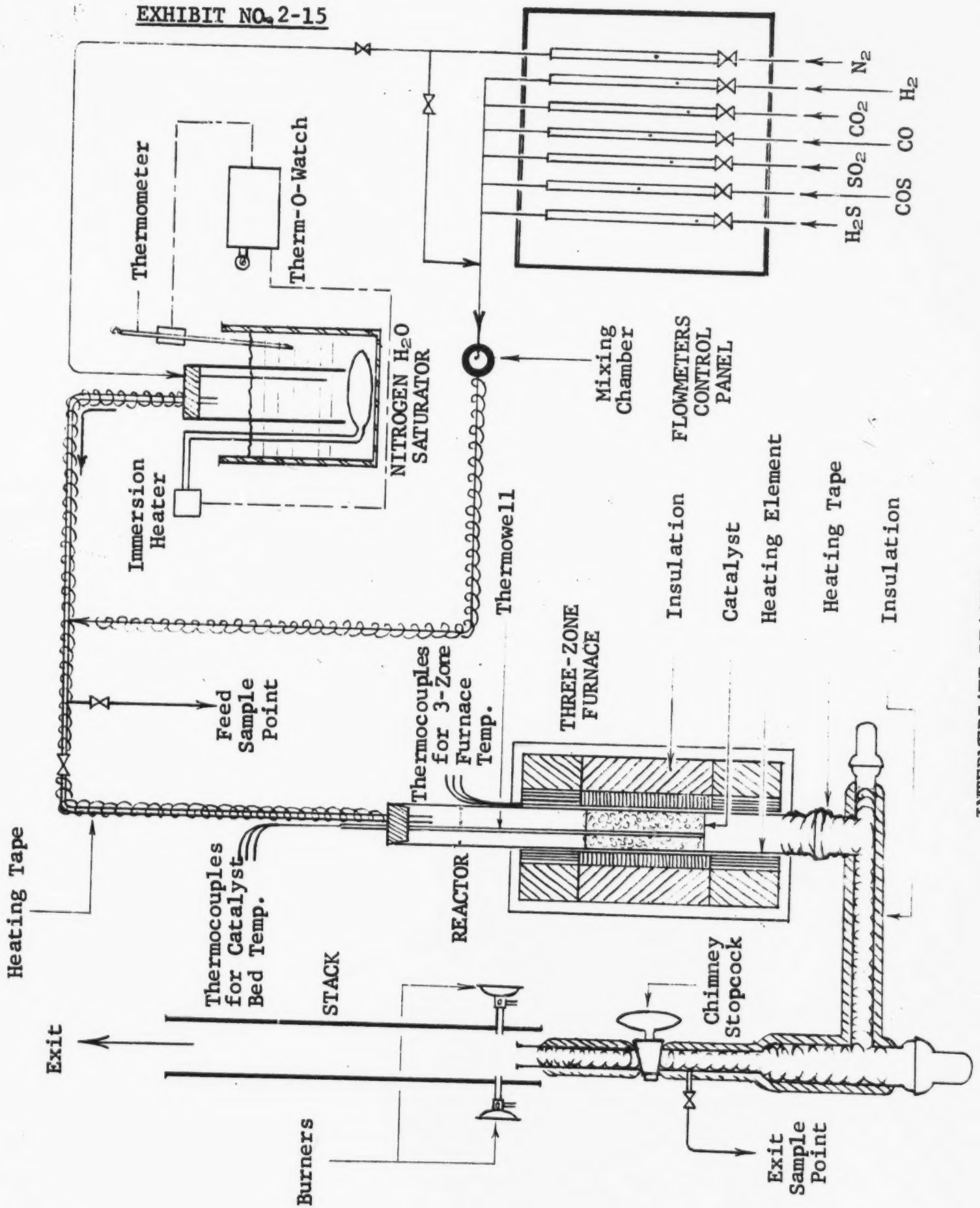
| Component        | Temp., °F    | Contact<br>Time, Sec. |
|------------------|--------------|-----------------------|
| COS:             | 662<br>842   | 1<br>1/2              |
| CO:              | 932<br>1022  | 1<br>1/2              |
| H <sub>2</sub> : | 1022<br>1112 | .3/2<br>1             |

EXHIBIT NO. 2-14

Typical Catalyst Bed  
Temperature Profiles

| Nominal<br>Temp.<br>°F | Actual Bed Temperature, °F    |      |      |      |      |      |      |
|------------------------|-------------------------------|------|------|------|------|------|------|
|                        | Bed Height from Bottom of Bed |      |      |      |      |      |      |
|                        | 0"                            | 2"   | 4"   | 5"   | 6"   | 8"   | 10"  |
| 662                    | 662                           | 658  | 658  | 662  | 666  | 671  | 667  |
| 752                    | 759                           | 761  | 756  | 752  | 756  | 759  | 757  |
| 842                    | 838                           | 838  | 842  | 842  | 851  | 849  | 842  |
| 932                    | 928                           | 928  | 928  | 932  | 932  | 936  | 932  |
| 1022                   | 1020                          | 1016 | 1018 | 1018 | 1022 | 1026 | 1022 |
| 1112                   | 1125                          | 1119 | 1112 | 1112 | 1112 | 1112 | 1112 |

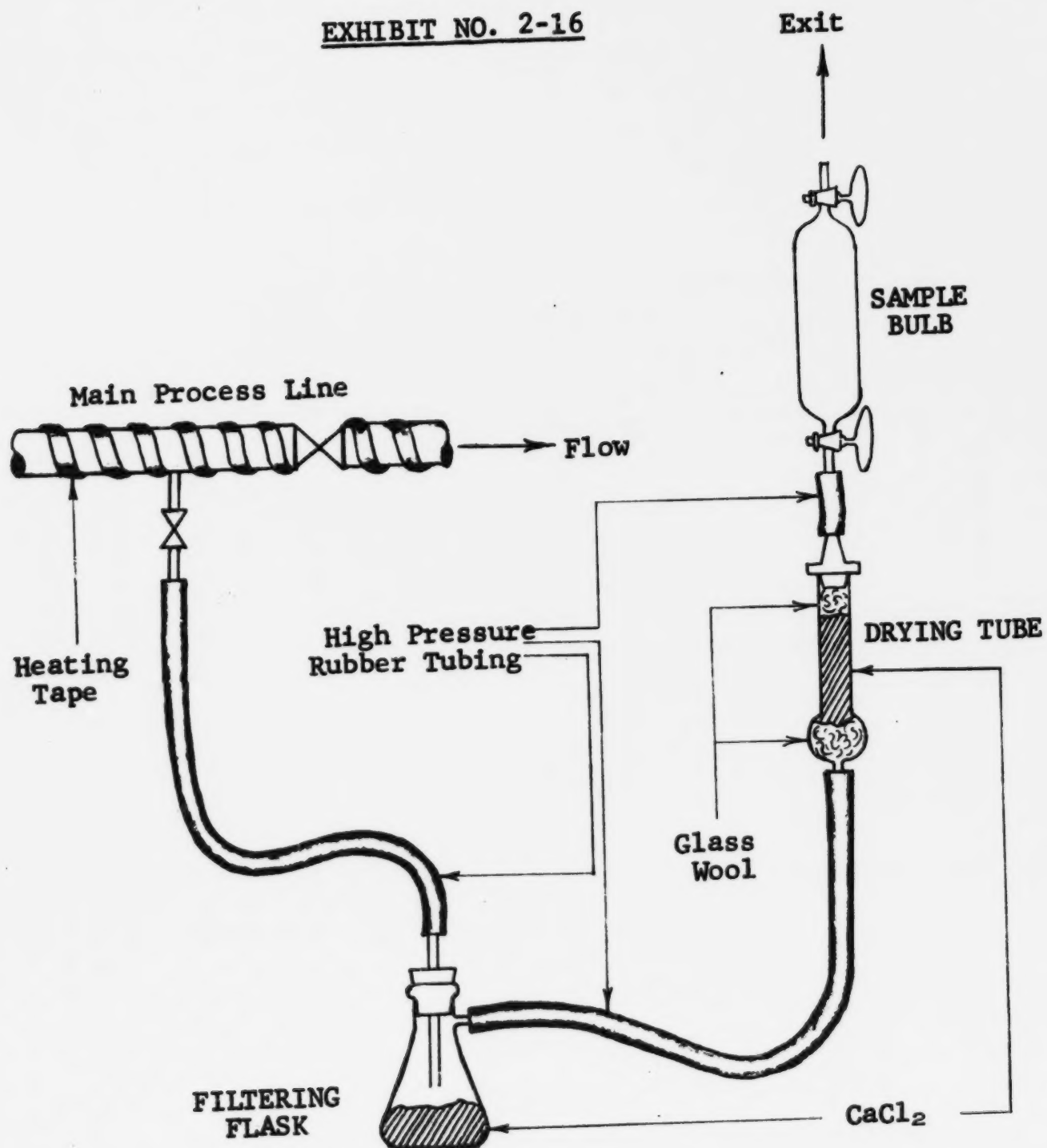
EXHIBIT NO. 2-15



INTERMEDIATE REACTOR  
EQUIPMENT SET-UP



EXHIBIT NO. 2-16



INTERMEDIATE REACTOR  
SAMPLING SYSTEM

3. LOW TEMPERATURE CLAUS STUDIES

3. LOW TEMPERATURE CLAUS STUDIES

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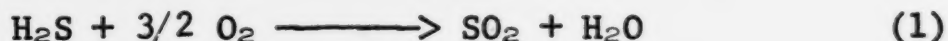


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### 3.1 INTRODUCTION

3.1.1 The classic Claus Process consists of burning one third of an  $H_2S$  stream completely to sulfur dioxide in a waste heat boiler and reducing this with the remaining two thirds  $H_2S$  over a catalyst, usually activated bauxite, at 400-650°F. The two stages of  $H_2S$  removal can be represented in the following way.



At these temperatures, sulfur is passed through the Claus reactor in the vapor phase and subsequently recovered in a sulfur condenser.

3.1.2 The low temperature Claus (LTC) process utilizes reaction (2) to reduce  $SO_2$  contained in stack gas to sulfur. The LTC process is distinguished from the conventional Claus by operation at a temperature low enough to inhibit oxygen reactions. This temperature was visualized to be below 400°F. At these temperatures the sulfur produced is assumed to be retained on the catalyst as solid or liquid sulfur. Preliminary calculations had indicated that a serious sulfur loss could occur if the sulfur on the catalyst was exhibiting its normal vapor pressure of the temperature range of the LTC process. This means that if a large loss as sulfur vapor is to be avoided, the catalyst must act as a sulfur vapor adsorbent as well as a catalyst. This is one assumption which had to be validated in the LTC laboratory program. Previous works had suggested that catalysts such as activated alumina were strong sulfur adsorbents. Information available at the time of conceptual process design also indicated that 20% sulfur by weight can be deposited on these catalysts before significant impairment of catalytic activity occurs. In the LTC process the sulfur, thus deposited, is then removed and the catalyst regenerated by heating to about 900°F and purging with an inert or reducing gas. The sulfur is recovered by cooling the purge stream and condensing the sulfur. One third of the sulfur is taken as product and the remaining two thirds is used to synthesize the  $H_2S$  required for the reduction process. The regenerated catalyst is recycled to process.  $H_2S$  can be synthesized with sulfur and  $H_2$ , or with sulfur, steam and  $CH_4$ . When  $CH_4$  is used as the reactant, the  $H_2S$  synthesis gases will contain small amounts of COS and  $CS_2$ . The  $H_2S$  efficiency in the LTC unit would be adversely effected if the COS and  $CS_2$  did not react to the same extent as  $H_2S$  reacts. The extent of COS and  $CS_2$  reaction is another aspect of process design

which would have to be investigated in the LTC laboratory program. Because 2/3 of the sulfur is recycled a high sulfur yield must be obtained within the LTC unit. A 97% yield from the Claus unit produces only a net sulfur yield of 91% from the entire system. The low temperatures of the LTC process do however favor a high equilibrium conversion (99%+), and high sulfur yields were anticipated.

3.1.3 Princeton Chemical Research Incorporated, previously contracted (Contract Number PH 86-68-43) to perform similar work with low concentration powerhouse stack gases. They conducted an extensive catalyst screening program from which we selected the prime catalyst candidates for our work.

3.1.4 Allied Chemical's principle concern with the LTC process was its possible applicability to the smelter situation, specifically copper smelting.

A typical copper smelter's stack analysis was taken as follows:

| <u>Component</u> | <u>Volume %</u> |
|------------------|-----------------|
| SO <sub>2</sub>  | 2.9             |
| O <sub>2</sub>   | 14.3            |
| CO               | 0.6             |
| CO <sub>2</sub>  | 1.7             |
| H <sub>2</sub> O | 0.1             |
| N <sub>2</sub>   | 80.4            |
|                  | <u>100.0</u>    |

Some 76% of SO<sub>2</sub> emissions of primary non-ferrous smelters are from copper smelters. Current public and governmental concern is high in the SO<sub>2</sub> pollution area and SO<sub>2</sub> emissions are increasing at an alarming rate. This points out the growing urgency for a useful SO<sub>2</sub> abatement process. In Phase I of Contract PH 22-68-24 Allied Chemical reviewed the technology of SO<sub>2</sub> abatement by reduction to sulfur techniques. At that time the low temperature Claus process appeared to be the most promising approach to the direct reduction of SO<sub>2</sub> in smelter gas.

3.1.5 Exhibits 3.1-1 and 3.1-2 illustrate one version of how LTC was visualized to be implemented for copper smelter stack gases. Exhibit 3.1-1 shows one modification of this process applied to our weakest smelter gas with 2.9 percent SO<sub>2</sub> and 14.3 percent oxygen. In this case, H<sub>2</sub>S is synthesized from sulfur and reformed methane in the equipment shown in the lower left of Exhibit 3.1-1. Half of the H<sub>2</sub>S is mixed with the smelter gas, and the mixture is then cooled to about 150°F by direct water injection prior



to entering the first of two stages in a moving catalyst bed type of reactor. The adiabatic heat rise of about 112°F necessitates further intercooling before the gas, mixed with the remaining half of the H<sub>2</sub>S, enters the second bed. Gases venting the reactor are incinerated and stacked.

Catalyst discharging from the reactor, containing about 20 percent sulfur by weight, is fed continuously to the regenerator, which operates at about 930°F. This is a multiple tube type heat exchanger with the catalyst inside the tubes. Heat is supplied by boiling sulfur and condensing the vapors on the outside of the tubes. An inert or reducing gas sweep is recycled through the regenerating catalyst mass and the sulfur recovery condenser.

Catalyst leaving the regenerator is cooled by an air sweep prior to re-entering the reactor. Somewhat over two thirds of the sulfur is recycled for H<sub>2</sub>S synthesis, and the remainder taken as product.

### 3.2 SUMMARY

3.2.1 The objective of the low temperature Claus program was to (1) verify assumptions and optimize conditions on a laboratory scale using a simulated smelter gas feed and (2) confirm the laboratory results on an actual smelter gas using similar, but portable, equipment. The LTC concept is based on reducing SO<sub>2</sub> with H<sub>2</sub>S in the presence of O<sub>2</sub> at a temperature where O<sub>2</sub> will not react in the system. To develop a usable process several aspects of process design had to be investigated and established. First the temperature at which the LTC reaction initiates had to be ascertained. The lowest operating temperature limit was set at the dew point of the gas mixture which was anticipated as feed for the Claus unit. The lower temperature limit for O<sub>2</sub> reactions also had to be established. The heat responses caused by water adsorption on the catalyst and its effect on reaction and reaction temperature was another important design consideration. If these heats imposed a significant temperature increase within the catalyst bed interfering O<sub>2</sub> reactions could ensue. The presence of NO<sub>x</sub> in smelter gas prompted an investigation on its effect on catalyst activity and its influence on subsequent yield. Activated alumina and molecular sieve were the prime catalyst candidates for the LTC process and their effectiveness and life characteristics had to be determined. The catalyst used must retain a high degree of catalytic activity. Successful LTC operation is based on no less than 97% conversion. Below this the process is inoperable from both an air pollution and economic standpoint.



3.2.2 A laboratory program was initiated to establish the salient aspects which comprise the design of a LTC process. One unique advantage of our laboratory work stemmed from design and use of a reactor system which behaved substantially adiabatically. Heretofore laboratory investigators utilized reactors which performed under apparent isothermal conditions. The adiabatic nature of our reactor system permitted the observation of several previously unobserved heat responses. Upon further investigation the LTC process was found unworkable because of the resultant myriad of complications. High temperature responses accompanied by interfering  $O_2$  reactions, a detrimental contribution from  $NO_x$  and subsequent loss of catalytic activity resulted in sulfur yield losses that rendered the LTC approach untenable. Consequently, the field tests were not carried out.

### 3.3 CONCLUSIONS

#### 3.3.1 Initiation Temperature

Low temperatures are reported to inhibit  $O_2$  reactions and favor sulfur yield in the LTC environment. It was felt previously that the high heat of reaction involved in the  $H_2S/SO_2$  reaction would cause the reaction to go to completion in the LTC operating range once it was initiated.  $120^\circ F$  was the lowest temperature considered because it approached the dew point of a visualized smelter gas feed stream (cooled by direct water injection). Fresh activated alumina was expected to be an active catalytic media over which reaction would initiate at a low temperature but with repeated catalyst use the initiation temperature was anticipated to rise. This change in initiation temperature was not experienced as the catalyst consistently initiated reaction at  $120^\circ F$ . Although only a limited time was spent with molecular sieve, the same consistency in reaction initiation at  $120^\circ F$  was experienced. Consequently we can conclude that all the catalysts studied, 1/4-1/2" Alcoa F-1, 1/4" Alcoa H-151 and 1/16" Linde molecular sieve 13X, will initiate the Claus reaction at  $120^\circ F$ .

#### 3.3.2 Heat Responses

The adiabatic temperature rise due to  $H_2S/SO_2$  reaction in a typical air-diluted smelter gas is approximately  $82^\circ F/\%$   $SO_2$  converted. This excludes other heat inducing variables such as water and sulfur adsorption on the catalyst. The actual temperature rise experienced was consistently higher than anticipated. These higher than anticipated temperatures increase the probability of  $O_2$  reactions, decrease the equilibrium conversion and increase the loss of sulfur values in the vapor phase. The net result of this inordinate temperature rise was an unacceptable sulfur yield loss which by itself makes LTC an inoperable process.

### 3.3.3 H<sub>2</sub>S/O<sub>2</sub> Reactions

One of the original premises upon which LTC was based was that H<sub>2</sub>S would not react with O<sub>2</sub> at LTC temperatures. This was proven false by passing H<sub>2</sub>S and O<sub>2</sub> through alumina catalyst. These were strong indications of O<sub>2</sub> reaction at temperatures as low as room temperature. Subsequent analyses of inlet and exit streams did show H<sub>2</sub>S oxidation does occur in the LTC range.

### 3.3.4 The Effect of NO<sub>x</sub>

The presence of 100 ppm NO<sub>x</sub> consistently had a detrimental effect on sulfur yield. This was true with SO<sub>2</sub> concentrations in both the smelter and power stack gas range. Thus NO<sub>x</sub> increased the already unacceptable yield loss due to temperature rises.

### 3.3.5 Catalyst Life

With continued use the catalytic activity of both Alcoa F-1 and H-151 decreased. After each run the catalyst was regenerated at 950°F by passing first a N<sub>2</sub> purge through the catalyst bed and then a N<sub>2</sub> purge stream containing 50% H<sub>2</sub>S. Catalyst activity loss is attributed to sulfate formation on the catalyst. H<sub>2</sub>S in the purge stream was intended to remove the sulfate by reduction to sulfur. This method of regeneration proved ineffective.

## 3.4 RECOMMENDATIONS

Data developed in this study show the LTC process for direct reduction of SO<sub>2</sub> in stack gases to be inoperative. It is recommended that no further work be done on this approach.

## 3.5 DATA AND DISCUSSION OF EXPERIMENTAL PROGRAM

### 3.5.1 Laboratory Apparatus Used

3.5.1.1 The reactor system (see Exhibit 3-2) consisted of a three inch diameter flanged stainless steel tube which contained the catalyst bed supported by a 1/4" mesh stainless steel grid. Four five inch 2100 watt band heaters, individually controlled with rheostats, furnished heat to the reactor. The temperature was monitored by four iron-constantan thermocouples which were strategically placed within an axial thermowell. The temperature was recorded on a Honeywell temperature recorder. The system

was well insulated and behaved substantially adiabatically at the low temperatures which were utilized. Gases were fed across the top of the reactor bed, passed through the catalyst bed, through the reactor's lower leg and subsequently through a combustion tube. The lower leg, fabricated from Vycor, was heated with heating tapes. This provided visual inspection for traces of elemental sulfur which escaped the catalyst bed. The temperature in the lower leg was monitored with an iron-constantan thermocouple and recorded on the Honeywell temperature recorder. The combustion tube was two inches in diameter and contained an eight inch bed of Alcoa F-1 activated alumina. It was heated with a twelve inch 3000 watt band heater and its shell temperature was also monitored. The combustion tube was maintained at 950°F to oxidize any sulfur gases which passed through the reactor. This served as a second monitor for any sulfur which might have broken through the reactor system, as gas analysis at this point would show an excess of SO<sub>2</sub> relative to the gases monitored directly after the reactor. The feed gases were metered by Fisher-Porter tri-flat rotameters. Air and nitrogen streams were passed through a humidifier to establish the necessary water concentration just prior to mixing with the sulfur bearing gases. Heating tapes provided heat to the lines between the humidifier and the reactor system. This prevented the possibility of water condensation in the lines. Three sample points were included, one at the inlet to the reactor tube, one at the reactor tube exit and one at the exit of the combustion tube. Samples were taken by passing the gas stream at the sample point through a drying media and through a 250 ml gas sampling bulb. The samples were then analyzed on a Perkin-Elmer Gas Chromatograph (Model 810) for H<sub>2</sub>S, SO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>.

### 3.5.2 Catalysts Used

3.5.2.1 Three different catalysts were used in the low temperature Claus program.

- (1) 1/4 inch Alcoa H-151 Activated Alumina.
- (2) 1/4 - 1/2 inch Alcoa F-1 Activated Alumina.
- (3) 1/16 inch Linde 13X Molecular Sieve.

These catalysts were chosen on the basis of previously reported work by others. The bulk of the work was done with the activated aluminas because of their comparative low cost. Linde molecular sieve underwent only a short test period because it induced higher temperatures and consequent lower sulfur yields than the aluminas. Both aluminas were almost equivalent in effectiveness although the H-151 consistently exhibited a more favorable temperature response.



### 3.5.3 Operational Procedure

#### Run Procedure

3.5.3.1 The catalyst bed temperature was stabilized by passing nitrogen, equivalent in volume to the run flow volume, through it and adjusting the band heaters to enforce the required temperature profile. This was performed with bone dry nitrogen except when the catalyst was preloaded with water.

3.5.3.2 After the catalyst bed had been stabilized, the nitrogen flow was replaced with the feed flow. Water was added to the feed stream by passing the nitrogen and air through a constant temperature water bath to produce the required water concentration. The lower reactor leg was maintained at 400°F to eliminate the possibility of sulfur buildup if the sulfur was not efficiently adsorbed in the catalyst bed. The combustion tube was maintained at 950°F to insure that any sulfur bearing gases would oxidize and exit as SO<sub>2</sub>. This served as a check against the possibility of elemental sulfur leaving the reactor system undetected. The gas chromatograph could easily analyze SO<sub>2</sub> whereas sulfur would have been condensed out in the sampling system and gone unnoticed.

3.5.3.3 Samples were taken and analyzed on the Perkin-Elmer 810 gas chromatograph periodically.

#### Regeneration Procedure

3.5.3.4 At the end of each run, if the catalyst was to be reused, it was regenerated. The temperature of the catalyst bed was regulated to 900-950°F by adjustment of the band heaters. A dry nitrogen purge stream of 300-500 cc/min was passed through the catalyst bed overnight (approximately 16 hours). A purge stream of 500-800 cc/min containing approximately 50% H<sub>2</sub>S was then passed through the catalyst for one half hour. During the entire regeneration procedure excess air was passed through the lower reactor leg and combustion tube to eliminate the possibility of molten sulfur buildup. The catalyst bed temperature was then reduced by passing approximately 60 liters per minute of dry nitrogen across the catalyst bed. It took several hours to cool the entire catalyst bed to operating conditions for the next run.

#### Sampling Procedure

3.5.3.5 Exhibit 3-3 illustrates the sampling apparatus used. At the start of each run a fresh supply of CaCl<sub>2</sub>, the drying agent used, was charged to the drying tube.



A 250 ml open ended gas sample bottle was connected to the end of the sampling line to collect a sample and the sampling valve was opened. The process gas was passed through the sample system for a 5 minute period prior to closing and removing the sample bulb. This guarded against the possibility of adsorption losses in the drying agent and insured a valid homogeneous sample in the sample bulb. The drying tube charge was changed after forty minutes of use. This prevented the  $\text{CaCl}_2$  from becoming spent.

#### 3.5.4 Advantages and Disadvantages of Apparatus

3.5.4.1 One of the outstanding advantages of the equipment was the adiabatic nature of the reactor. This permitted the observance of heat responses which had been previously overlooked with smaller and poorly insulated reactors. Smaller equipment has a tendency to operate isothermally. Once the catalyst bed temperature had been stabilized it remained constant until influenced by internal reaction and adsorption phenomenon. The temperature was monitored and recorded continuously at three points in the catalyst bed. Another advantage was the adaptability to variance in feed conditions which the system had. It operated with  $\text{SO}_2$  feed concentrations varying from 0.3 to 3.0 percent.

3.5.4.2 The major disadvantage of the apparatus was that its size and adiabatic nature made temperature control difficult. It took time for the band heaters to heat the three inch diameter bed uniformly. Also the catalyst bed's adiabatic nature caused cooling to take an even longer time. Because of this slow temperature response to cooling runs could not always be performed as often as desired.

#### 3.5.5 Comparisons with Previously Reported Data

##### Princeton Chemical Research, Inc.

3.5.5.1 Princeton Chemical Research was contracted (Contract Number PH 86-68-48) by the Department of Health, Education and Welfare for the Development of Processes to Reduce Sulfur Dioxide to Elemental Sulfur. PCR became involved in low temperature Claus as it applied to a typical power stack gas. Power stack gas generally contains approximately 0.3%  $\text{SO}_2$  by volume as compared to approximately 3.0% contained in air-diluted mixture of reverberatory and converter exits in a copper smelter.

3.5.5.2 Several catalyst were screened by PCR. Linde molecular sieve 13X, Alcoa F-1 alumina and Alcoa H-151 alumina were found to be among the best overall performers. It is these catalysts which were used in Allied's LTC program.

3.5.5.3 PCR performed their experimentation in a one inch reactor with a 1/4" axial thermowell as compared with the three inch reactor which Allied used. PCR used only about 15 grams of catalyst while Allied used approximately 1700 grams. The considerably smaller size of the PCR apparatus gave them the capability of running their experimentation at a rapid pace. Allied felt a larger reactor would be advantageous in obtaining realistic data. The larger equipment effectively operated adiabatically, as previously reported, and it is primarily this feature that allowed measurement of heat responses, heretofore unobserved, that resulted in concluding the LTC process unacceptable. It should be noted, however, that heat release due only to  $H_2S + SO_2$  reaction in the 0.3%  $SO_2$  range is small and would be inconsequential if water, oxygen, and  $NO_x$  were not present.

#### Consolidation Coal Company

3.5.5.4 Consolidation Coal presented a paper at the September 1969 meeting of the American Chemical Society entitled "Removal of Sulfur Dioxide from Power Plant Stacks by a Modified Claus Process". Their work parallels that of Princeton Chemical Research, Inc.

3.5.5.5 The catalysts which they used were quite similar to catalysts used both by Allied and PCR - high surface area activated aluminas.

3.5.5.6 Consolidation Coal used a reactor tube 34 mm (1 1/3 inches) in diameter with an axial thermowell. The catalyst bed was one to three inches in height as compared with Allied's 3 inch diameter reactor tube with a 15 inch catalyst bed. Consequently the apparatus used is much more similar in size and application to that of PCR and has the same disadvantages and advantages associated with it.

#### 3.5.6 Initiation Temperature

3.5.6.1 Exhibit 3-4 demonstrates that the  $H_2S-SO_2$  reaction does initiate over alumina catalyst as low as 120°F. Runs 11, 14 and 17 all resulted in an appreciable temperature response. Exit analysis also indicated a considerable reduction in both  $H_2S$  and  $SO_2$ .

### 3.5.7 Heat Responses

3.5.7.1 The temperature rise in the catalyst bed was not anticipated to exceed the adiabatic temperature rise due to reaction alone. The adiabatic temperature rise, approximately 82°F/% SO<sub>2</sub> reacted was calculated as illustrated in Appendix 3-1.

3.5.7.2 In the smelter gas range the temperature rise in a single bed is excessive and staging with intercooling on a commercial unit would be required. The adiabatic temperature rise in a smelter gas containing 3% SO<sub>2</sub> would be 3 X 82°F or 246°F. This temperature rise would have an adverse effect on equilibrium and most probably induce oxygen reactions. Exhibit 3-5 illustrates this staging requirement. In run 4 a 6.0% H<sub>2</sub>S - 3.0% SO<sub>2</sub> stream was fed over F-1 alumina at 260°F in the presence of O<sub>2</sub>. Within five minutes the temperature had already risen to 650°F. At this point the feeds were stopped to curtail reaction. On a commercial scale this catastrophic temperature rise would prove damaging not only in terms of conversion but also in terms of equipment. Runs 5 and 7 repeat this 6.0% H<sub>2</sub>S - 3.0% SO<sub>2</sub> feed without O<sub>2</sub>. The temperature rise is prohibitive as far as yield is concerned but certainly not the drastic temperature rise experienced with O<sub>2</sub>. In run 4 we were obviously experiencing oxygen reactions. The temperature change in run 7 is greater than that experienced in run 5. This may be due to the fact that there was more sulfur condensation and adsorption at the lower initial bed temperature, 150°F as compared with 260°F.

3.5.7.3 Exhibit 3-6 demonstrates that O<sub>2</sub> does effect temperature excursions in the Claus environment. In runs 20-24 approximately 15% O<sub>2</sub> replaces N<sub>2</sub> 28 minutes into the run. In each instance there is an immediate temperature response. This implies that oxygen reactions are proceeding.

3.5.7.4 Noteworthy is the fact that the adiabatic temperature rise as calculated is not inclusive in that it does not account for temperature rises due to adsorption phenomenon, especially water and sulfur. R. E. Derr of Alcoa in an article in Industrial and Engineering Chemistry in April 1938 discussed the use of activated alumina as a drying agent. He states:

In the adsorption of 1 pound of moisture from any gas, heat approximately equivalent to the condensation of one pound of steam is liberated. If air containing 7 grains of moisture per cubic foot is being dried, then about 1000 BTU



will be converted for every 1000 cubic foot of air dried. This is sufficient to raise the temperature of air, at normal pressure, about 30°C (54°F). One might expect that the temperature of the dry exit gas would immediately show a corresponding rise, but this is not the case. The alumina stores the heat in the zone where adsorption at high efficiency is taking place, and the temperature of the exit gas remains below the calculated figure throughout more than half the adsorption period. The temperature of the exit then rises above the mean temperature, but adsorption at high efficiency continues until the exit gas approaches its maximum temperature.

3.5.7.5 As Derr indicates water is a significant heat contributor and we can infer that this heat would be realized in the operation of the low temperature Claus unit. Indeed the heat responses that were typical in our low temperature Claus system passed through the reactor in the same manner as Derr explained. Exhibit 3-7 illustrates the typical heat response exhibited across the low temperature Claus unit with time. This type of heat response was exhibited whenever there was heat liberated as a result of passing gas through the catalyst bed. Exhibit 3-8 demonstrates that the heat liberated due to water adsorption is significant. Runs 1-3 utilize Alcoa F-1 alumina (1/4-1/2"). As the length of the run was extended more of the catalyst bed exhibited a heat response. The catalyst used in run 1 was dehydrated by passing a N<sub>2</sub> purge through it at 300°F for 1/2 hour. This proved to be an ineffective method for dehydration as run 2 demonstrated (the top of the catalyst bed saw only a 95°F temperature rise as compared with 150°F in run 1). The catalyst used in run 2 was then dehydrated at 500°F for 1/2 hour. The temperature response at the top of catalyst bed in run 3, 125°F, showed that 500°F is much more effective in terms of dehydration. Runs 8 and 9 utilized Alcoa H-151 (1/4"). The contact time was decreased from 7.1 seconds (superficial at S.T.P.) to 2.0 seconds. As might be expected a decrease in contact time was reciprocated with an increase in the rate of temperature response. One can draw the conclusion that the rate of temperature response is inversely proportional to the contact time. Because the H-151 and F-1 aluminas are so similar in nature, this increase in the rate of temperature response is not due to differences in the two aluminas. In Run 9 13% or approximately four times the water concentration as in run 8 was fed into the reactor. An interesting observation is that although both catalyst bed attain approximately the same maximum temperature,



run 8 achieves it approximately four times faster. It may be concluded from this that the rate of temperature response is directly proportional to inlet water concentration under these operating conditions.

3.5.7.6 The recognition that the heat of water adsorption on alumina catalyst is appreciable prompted the following speculation:

Use of dry, regenerated catalyst can give a heat rise which will be the sum of the heat of reaction and the heat of adsorption of water. This can be true even if dry gases are reacted, since water is formed in the reaction. This additive effect probably can be avoided if the catalyst, after regeneration is loaded with water and cooled prior to the reaction. Again, if a cooled water-loaded catalyst is used, it is just possible that the sulfur being retained in the catalyst will tend to displace the adsorbed water. Since heat effects are reversible, this would provide cooling that would counteract the heat of reaction. Indeed preliminary calculations indicate that with a 15 percent water loading on the alumina, and a subsequent 20 percent loading with sulfur, the system would be substantially isothermal regardless of the  $\text{H}_2\text{S}$ - $\text{SO}_2$  concentration. However, the phenomena of water displacement by sulfur adsorption must occur, otherwise this concept will not work.

3.5.7.7 Exhibit 3-9 tabulates our work in this area.

In each instance water-saturated nitrogen was fed across the catalyst bed until the bed temperature stabilized at the prescribed initial bed temperature for that particular run. It generally took several hours for the catalyst bed temperature to stabilize. In run 6 a 6.0%  $\text{H}_2\text{S}$ -3.0%  $\text{SO}_2$  stream was fed across water presaturated F-1 alumina at 150°F. A temperature rise up to 425°F was experienced. The phenomenon of water displacement by sulfur adsorption obviously did not induce isothermal conditions in run 6. In runs 12 and 13 run 5 was repeated with a 3.0%  $\text{H}_2\text{S}$ -1.5%  $\text{SO}_2$  feed stream at a lower initial bed temperature. The thought was that a lower temperature alumina may retain enough additional water to induce isothermal conditions. Runs 12 and 13 exhibited very little temperature change, 35°F maximum, but the exit analysis indicated very little reaction taking place. Run 14 repeated runs 12 and 13 but using a dry catalyst bed. This would ascertain if the catalyst had somehow become poisoned. A high temperature response and a much higher yield with the

dry catalyst was noted. Identical results were attained in runs 15, 16 and 17, showing both low temperature and low yield responses with a water presaturated catalyst and substantially the opposite with a dry catalyst. It was concluded from this series of runs that water presaturation at 120°F deactivates the catalyst.

3.5.7.8 Exhibit 3-10 demonstrates why high sulfur yields in the Claus reactor are important. Because two thirds of the sulfur produced is recycled to the reactor system a 97% yield in the Claus reactor produces a net yield loss of approximately 9%. Exhibit 3-11 illustrates how yield loss was experimentally determined. Exit samples were taken during each run and plotted as pound sulfur per minutes versus time. The area under this curve was then computed and compared with the pounds sulfur which would have been collected on the catalyst at 100% conversion.

### 3.5.8 H<sub>2</sub>S/O<sub>2</sub> Reactions

3.5.8.1 Several runs were performed to establish the temperature threshold at which H<sub>2</sub>S oxidation occurs. This is important because the LTC process is based on operating in a temperature regime where reaction interference from O<sub>2</sub> is insignificant. Activated alumina catalysts (F-1 and H-151) were utilized in these tests as they appeared to be the prime candidate for the LTC reaction. Both regenerated and fresh alumina were tested in the following manner. H<sub>2</sub>S and N<sub>2</sub> were passed across the alumina, heated by the reactor band heaters, thereby stabilizing the temperature of the catalyst bed. O<sub>2</sub> in the form of air was then substituted for a portion of the nitrogen establishing a 15% O<sub>2</sub> content in the feed. Samples were collected and analyzed at the inlet and exit and the temperature in the catalyst bed was monitored throughout the run. Exhibit 3-12 tabulates the feed and resultant response in several runs. Exhibit 3-13 compares the average analysis of sulfur bearing streams into and out of the catalyst bed. In each instance an immediate temperature rise occurred indicating an exothermic reaction was proceeding on the alumina. In most cases the exit stream contained both H<sub>2</sub>S and SO<sub>2</sub> and the total of the sulfur bearing gases exiting the bed was not equivalent to the H<sub>2</sub>S entering the bed. This implies that the formation of sulfur did take place across the alumina. The reduction of H<sub>2</sub>S in the exit stream can be accounted for by combinations of the following reactions:



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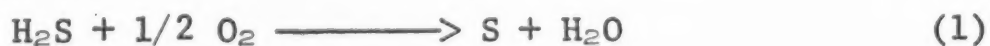


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3.5.8.2 In runs 28-31 regenerated H-151 alumina was used. At the inlet temperature of 100°F in run 29 59% of the H<sub>2</sub>S passed through the reactor with the bulk of the difference being converted to sulfur. This was accompanied by a maximum temperature change of 105°F. In run 30 with an inlet temperature of 130°F similar results were attained. Only 1% of the H<sub>2</sub>S passed through the reactor unreacted in run 31, which had an inlet temperature of 205°F. 67% went to SO<sub>2</sub> and the remainder to sulfur. The maximum temperature change realized was 715°F. Run 28 demonstrates that at 315°F essentially all of the H<sub>2</sub>S was converted to SO<sub>2</sub>.

3.5.8.3 In summation, the following can be deduced about the net reactions occurring with regenerated H-151 alumina:

- (a) Above 315°F, only reaction (4) takes place.
- (b) Above 205°F reaction (4) dominates.
- (c) Somewhere below 205°F reaction (1) dominates.

3.5.8.4 In runs 69-70 fresh H-151 alumina was used. In run 69 the inlet temperature was 75°F and the maximum temperature change experienced was 825°F. Exit analysis indicated that 45.5% of the H<sub>2</sub>S feed was converted to SO<sub>2</sub>, 12.5% remained unreacted and the balance went to sulfur. At a inlet temperature of 150°F, 69.5% of the H<sub>2</sub>S went to SO<sub>2</sub>, 3% did not react and 27.5% was converted to sulfur. The maximum temperature change in the catalyst bed was 830°F. The implication here is that fresh H-151 is more reactive than regenerated H-151. The predominate net reaction occurring was reaction (4).

3.5.8.5 Fresh F-1 alumina was used in runs 65-67. The inlet catalyst bed temperature in run 65 was 75°F, in run 66 it was 165°F and in run 67, 250°F. Sulfur was deposited on the catalyst by running a preliminary short term LTC reaction on the catalyst used in runs 66 and 67. The presence of sulfur would demonstrate whether or not sulfur would be stripped from the catalyst if H<sub>2</sub>S reactions did occur. In run 65 more than half (53%) of the H<sub>2</sub>S passed through the catalyst bed unreacted, the balance forming sulfur. In both runs 66 and 67 the major reaction which took place was reaction (4). The analyses also indicated that reaction(2) also took place to a significant degree. The temperature response in both runs 66 and 67 registered off the recorder scale (in excess of 945°F). From these runs it can be concluded that if H<sub>2</sub>S oxidation does occur to an appreciable extent, sulfur on the catalyst will also be oxidized. Also, at 75°F H<sub>2</sub>S oxidizes predominantly to sulfur and at 165°F and above, predominantly to SO<sub>2</sub>.

### 3.5.9 Effect of NO<sub>x</sub>

3.5.9.1 Smelter gases contain minute amounts of NO<sub>x</sub> and its presence has been found to promote sulfate formation on alumina catalysts causing a loss of catalyst activity. Exhibit 3-14 demonstrates that the presence of only 100 ppm NO<sub>x</sub> consistently induces a detrimental effect on LTC yields. Also the smaller the inlet concentration of H<sub>2</sub>S and SO<sub>2</sub> the more significant is the NO<sub>x</sub> deactivation phenomenon.

3.5.9.2 0.6% H<sub>2</sub>S and 0.3% SO<sub>2</sub> were passed across H-151 alumina in runs 35, 38 and 45. No NO<sub>x</sub> was present and the average yield loss is 12.7%. Identical runs 36, 37 and 46 with NO<sub>x</sub> present in the feed resulted in a 26.2% yield loss. With a 1.2% H<sub>2</sub>S/0.6% SO<sub>2</sub> feed 25.0% yield loss was realized with NO<sub>x</sub> and 17.0% without (runs 43 and 44). At the 3.0% H<sub>2</sub>S·1.5% SO<sub>2</sub> concentration level (runs 32, 33, 34 and 40) an average yield loss of 18.4% was experienced without NO<sub>x</sub> and 26.0% with NO<sub>x</sub> present.

### 3.5.10 Catalyst Life

3.5.10.1 To make the LTC operation a viable process the catalyst used must be capable of being stripped of sulfur and rejuvenated to its original state of activity. Following each run the alumina was heated to 900°F+ and a N<sub>2</sub> purge was passed across it to remove the sulfur. Next a purge stream containing 50% H<sub>2</sub>S was passed through the catalyst bed to reduce sulfate formed in the LTC reaction. This regeneration procedure had reportedly been used successfully in prior work. This procedure, however, did not reactivate the catalyst to its previous state as indicated in Exhibit 3-15.

3.5.10.2 In run 41 fresh H-151 alumina was used. After 15 hours use, which involved four regenerations, two duplicate runs were made (runs 45 and 46). In each instance the yield loss was increased significantly. A repeat of this procedure was made with F-1 alumina. In run 47 yield loss over fresh F-1 was effectively zero. After ten regenerations and 26 hours use two identical runs (runs 57 and 58) produced an 8-10% yield loss.

## 3.6 REFERENCES

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3. British Patent 1,132,846, issued to Peter Spence, LTD, 11/6/68.
4. Arthur G. McKee Company. Systems Study for Control of Emissions. Primary Nonferrous Smelting Industry, for NAPCA, Contract No. PH 86-65-85, May 1969.
5. R. T. Struck et al, (Consolidation Coal Co.), "Removal of Sulfur Dioxide by a Modified Claus Process", presented at ACS meeting of September 1969.
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## H<sub>2</sub>S REDUCTION OF SO<sub>2</sub> LOW TEMPERATURE CLAUSE





EXHIBIT NO. 3-1-2

Low Temperature Claus

210000 SCFM 2C Smelter Gas

| Process Points     | A      | B      | C     | D     | E     | F     | K     | L     | M      | N     | O      | P      | Q      | R     | S      | T      | U      | V      | W     |
|--------------------|--------|--------|-------|-------|-------|-------|-------|-------|--------|-------|--------|--------|--------|-------|--------|--------|--------|--------|-------|
| Temp. °C           | 25     | 205    | 898   | 300   | 625   | 300   | 540   | 125   | 227    | 125   | 223    | 65     | 115    | 125   | 116    | 65     | 115    | 125    | 420   |
| SCFM               | 3073   | 9217   | 18320 | 19850 | 19300 | 19300 | 18640 | 18580 | 210000 | 9290  | 219290 | 243290 | 234200 | 9290  | 243490 | 252540 | 249500 | 1000   | 3160  |
| CFM at T°C         | 3360   | 16140  | 78570 | 41690 | 63480 | 40530 | 55510 | 27090 | 384720 | 13540 | 398450 | 301190 | 332800 | 13540 | 346980 | 312640 | 354540 | 1460   | 8020  |
| Dew Point °C       |        |        |       |       |       |       |       |       |        |       |        | 47.5   |        |       |        | 53.4   |        |        |       |
| % CH <sub>4</sub>  | 100.00 |        | 0.35  | 0.32  | 0.11  | 0.11  | 16.74 | 16.80 | 0.10   | 16.80 | 0.81   | 10.60  | 11.01  | 16.80 | 11.23  | 14.40  | 16.98  |        |       |
| % H <sub>2</sub> O |        | 100.00 | 29.03 | 26.78 | 19.03 | 19.03 | 0.11  | 0.11  | 0.60   | 0.11  | 0.58   | 0.52   | 0.54   | 0.11  | 0.53   | 0.51   | 0.51   |        |       |
| % CO               |        |        | 11.57 | 10.68 | 3.96  | 3.95  | 1.31  | 1.31  | 1.70   | 1.31  | 0.05   | 0.05   | 0.05   | 1.31  | 0.10   | 0.10   | 0.10   |        |       |
| % H <sub>2</sub>   |        |        | 54.20 | 50.00 | 19.05 | 19.05 | 16.17 | 16.23 | 1.70   | 16.23 | 2.32   | 2.09   | 2.17   | 16.23 | 2.70   | 2.61   | 2.67   |        |       |
| % CO <sub>2</sub>  |        |        | 4.85  | 4.48  | 10.53 | 10.53 | 0.34  | 0.34  | 0.34   | 0.34  | 0.02   | 0.02   | 0.00   | 0.34  | 0.02   | 0.02   | 0.00   |        |       |
| % COS              |        |        |       |       | 0.15  | 0.15  | 64.98 | 65.21 | 65.21  | 65.21 | 2.76   | 2.50   | 0.00   | 65.21 | 2.50   | 2.40   | 0.024  |        |       |
| % H <sub>2</sub> S |        |        |       |       | 35.69 | 35.69 | 0.34  | 0.00  |        | 0.00  |        |        |        |       |        |        |        |        | 37.70 |
| % S <sub>2</sub>   |        |        |       | 7.74  |       |       |       |       |        |       |        |        |        |       |        |        |        |        | 30.80 |
| % S <sub>8</sub>   |        |        |       |       |       |       |       |       | 2.90   |       | 2.78   | 2.50   | 1.31   |       | 1.26   | 1.21   | 0.012  |        |       |
| % SO <sub>2</sub>  |        |        |       |       |       |       |       |       | 14.30  |       | 13.68  | 12.34  | 12.82  |       | 12.33  | 11.89  | 12.03  |        |       |
| % O <sub>2</sub>   |        |        |       |       |       |       |       |       | 80.40  |       | 77.00  | 69.38  | 72.08  |       | 69.34  | 66.86  | 67.67  | 100.00 |       |
| % N <sub>2</sub>   |        |        |       |       |       |       |       |       |        |       |        |        |        |       |        |        |        |        | 31.50 |

| Point | Temp. °C |
|-------|----------|
| G     | 300      |
| H     | 250      |
| ZA    | 100      |
| ZB    | 75       |
| ZC    | 400      |

Conversion

Equilibrium 99.63%  
Used Here 99.50%

Sulfur Yield 98.52%  
Methane Factor 11490 SCF/Ton S  
Catalyst Circulation Rate 194.4 Ton/Hr.

| Point | Sulfur Distribution | N.T./Day |
|-------|---------------------|----------|
| X     | From Catalyst       | 1166.72  |
| I     | From Gas Cooler     | 9.15     |
|       | Total S Recovery    | 1174.87  |
| J     | Recycle Sulfur      | 789.83   |
| Y     | Net S Recovery      | 385.04   |

EXHIBIT 3-2

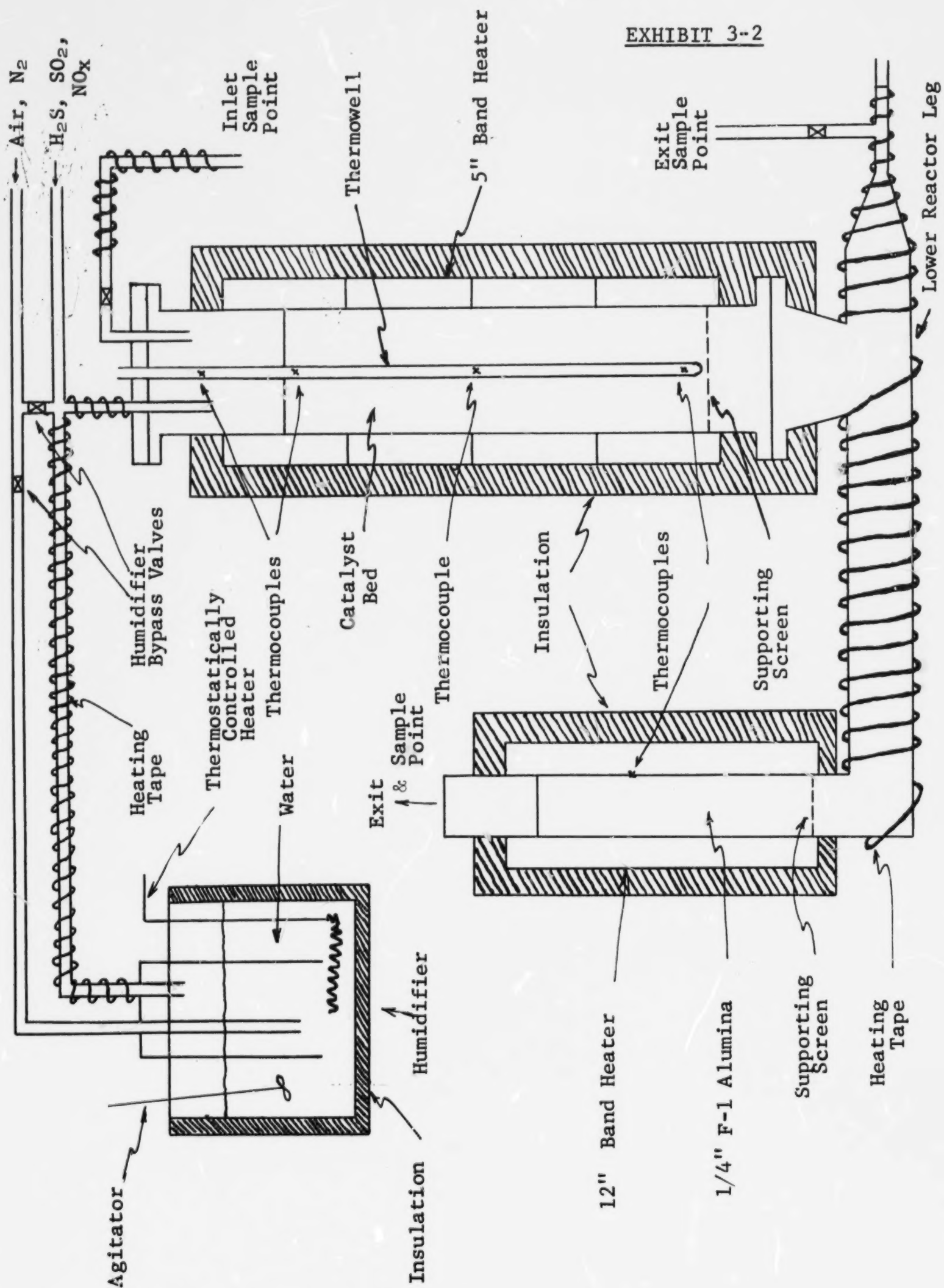
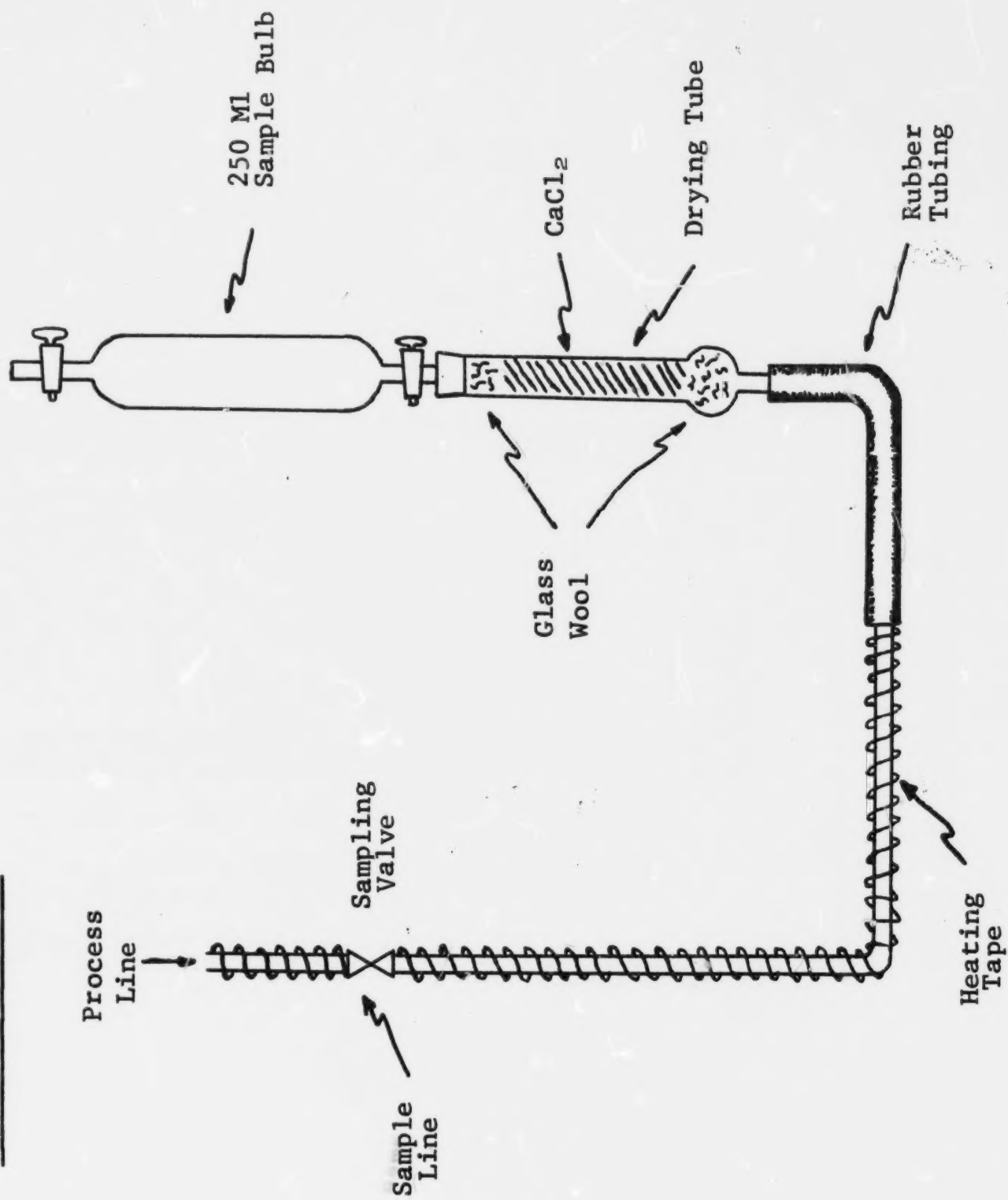


EXHIBIT 3-3  
SAMPLING APPARATUS



# EXHIBIT 3-4

TABULATION DEMONSTRATING H<sub>2</sub>S/SO<sub>2</sub> INITIATION TEMPERATURE

| Run No. | % H <sub>2</sub> S | % SO <sub>2</sub> | % N <sub>2</sub> | % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) | Total Flow (L/min.) | Initial Bed Temp. (°F) | Contact Time (sec.) | Duration of Run (min.) | Catalyst Used | ΔT Max. Top (°F) | ΔT Max. Middle (°F) | ΔT Max. Bottom (°F) | Max. Temp. (°F) |
|---------|--------------------|-------------------|------------------|------------------|--------------------|-----------------------|---------------------|------------------------|---------------------|------------------------|---------------|------------------|---------------------|---------------------|-----------------|
| 11      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 75                     | Regen. H-151  | 100              | 190                 | 170                 | 310             |
| 14      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 165                    | Regen. H-151  | 80               | 185                 | 190                 | 310             |
| 17      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 130                    | Regen. H-151  | 110              | 220                 | 200                 | 340             |

# EXHIBIT 3-5

TABULATION DEMONSTRATING THE NEED FOR STAGING

| Run No. | % H <sub>2</sub> S | % SO <sub>2</sub> | % N <sub>2</sub> | % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) | Total Flow (L/min.) | Initial Bed Temp. (°F) | Contact Time (sec.) | Duration of Run (min.) | Catalyst Used | ΔT Max. Top (°F) | ΔT Max. Middle (°F) | ΔT Max. Bottom (°F) | Max. Temp. (°F) |
|---------|--------------------|-------------------|------------------|------------------|--------------------|-----------------------|---------------------|------------------------|---------------------|------------------------|---------------|------------------|---------------------|---------------------|-----------------|
| 4       | 6.0                | 3.0               | 73.8             | 10.0             | 7.2                | None                  | 51.2                | 260                    | 2.0                 | 5                      | Dehyd. F-1    | 390              | -                   | -                   | 650             |
| 5       | 6.0                | 3.0               | 83.8             | None             | 7.2                | None                  | 51.2                | 260                    | 2.0                 | 105                    | Regen. F-1    | 115              | 215                 | 116                 | 480             |
| 7       | 6.0                | 3.0               | 80.4             | None             | 10.                | None                  | 51.2                | 150                    | 2.0                 | 110                    | Regen. F-1    | 230              | 275                 | 275                 | 425             |



EXHIBIT 3-6

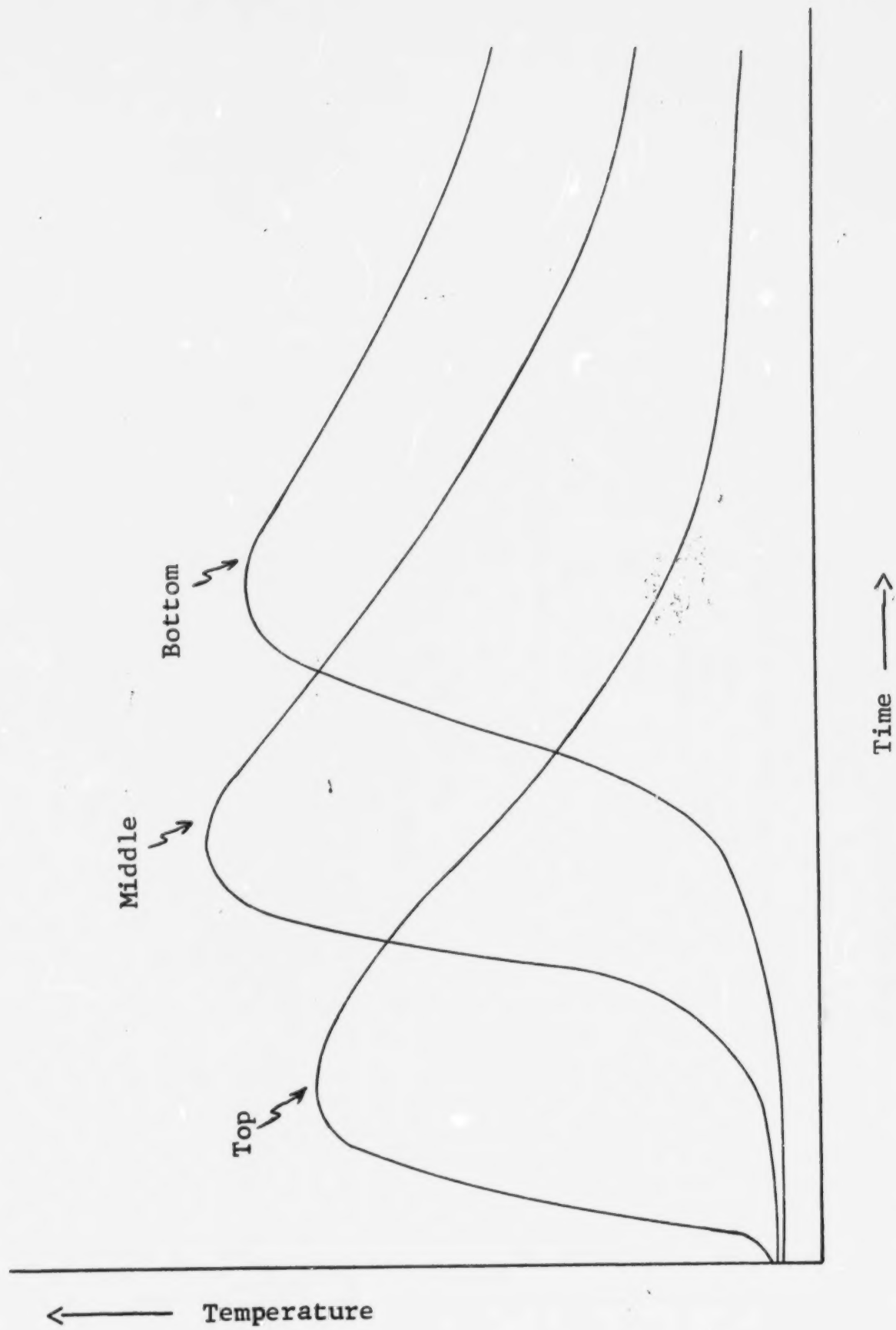
EFFECT OF OXYGEN CONTENT ON TEMPERATURE EXCURSIONS

| Run No. | % H <sub>2</sub> S | % SO <sub>2</sub> | % N <sub>2</sub> | * % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) | Total Flow (L/min.) | Initial Bed Temp. (°F) | Contact Time (sec.) | Duration of Run (min.) | Catalyst Used | ΔT Max.* Top (°F) | ΔT Max.* Middle (°F) | ΔT Max.* Bottom (°F) | Max. Temp. (°F) |
|---------|--------------------|-------------------|------------------|--------------------|--------------------|-----------------------|---------------------|------------------------|---------------------|------------------------|---------------|-------------------|----------------------|----------------------|-----------------|
| 20      | 3.0                | 1.5               | Bal.             | 15.0               | 10.0               | None                  | 51.4                | 120                    | 2.0                 | 80                     | Regen. H-151  | 10                | 40                   | 30                   | 360             |
| 21      | 3.0                | 1.5               | Bal.             | .0                 | 10.0               | 100                   | 51.4                | 120                    | 2.0                 | 75                     | Regen. H-151  | None              | 30                   | 50                   | 370             |
| 22      | 3.0                | 1.5               | Bal.             | 15.0               | 10.0               | None                  | 51.4                | 150                    | 2.0                 | 72                     | Regen. H-151  | 10                | 65                   | 90                   | 390             |
| 23      | 3.0                | 1.5               | Bal.             | 15.0               | 10.0               | 100                   | 51.4                | 150                    | 2.0                 | 60                     | Regen. H-151  | 20                | 135                  | 235                  | 545             |
| 24      | 3.0                | 1.5               | Bal.             | 15.0               | 10.0               | None                  | 51.4                | 170                    | 2.0                 | 75                     | Regen. H-151  | 15                | 165                  | 265                  | 585             |

\* -ΔT max. measured from temperature achieved after 28 minutes into run.  
At this point O<sub>2</sub> is added.

EXHIBIT 3-7

TEMPERATURE RESPONSES THROUGH THE CATALYST BED WITH TIME



# EXHIBIT 3-8

TABULATION DEMONSTRATING THE HEAT INDUCED BY WATER ADSORPTION

| Run No. | % H <sub>2</sub> S | % SO <sub>2</sub> | % N <sub>2</sub> | % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) | Total Flow (L/min.) | Initial Bed Temp. (°F) | Contact Time (sec.) | Duration of Run (min.) | Catalyst Used | ΔT Max. Top (°F) | ΔT Max. Middle (°F) | ΔT Max. Bottom (°F) | Max. Temp. (°F) |
|---------|--------------------|-------------------|------------------|------------------|--------------------|-----------------------|---------------------|------------------------|---------------------|------------------------|---------------|------------------|---------------------|---------------------|-----------------|
| 1       | None               | None              | 89.4             | None             | 10.6               | None                  | 7.2                 | 120                    | 7.1                 | 60                     | Fresh F-1     | 150              | None                | None                | 270             |
| 2       | None               | None              | 89.4             | None             | 10.6               | None                  | 7.2                 | 120                    | 7.1                 | 60                     | Dehyd. F-1    | 95               | None                | None                | 215             |
| 3       | None               | None              | 89.4             | None             | 10.6               | None                  | 7.2                 | 120                    | 7.1                 | 340                    | Dehyd. F-1    | 125              | 115                 | 100                 | 245             |
| 8       | None               | None              | 97.0             | None             | 3.0                | None                  | 51.2                | 120                    | 2.0                 | 100                    | Fresh H-151   | 35               | 115                 | 100                 | 235             |
| 9       | None               | None              | 87.0             | None             | 13.0               | None                  | 51.2                | 120                    | 2.0                 | 100                    | Dehyd. H-151  | 60               | 115                 | 85                  | 235             |

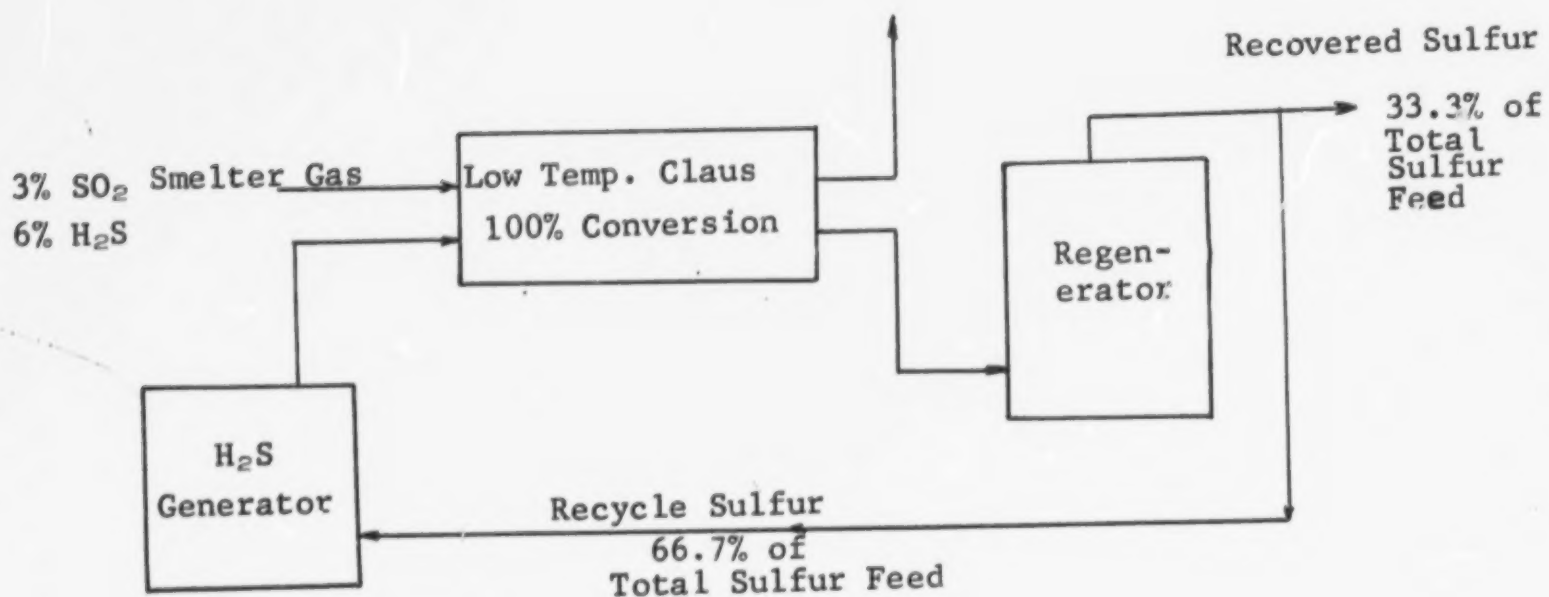
# EXHIBIT 3-9

TABULATION DEMONSTRATING THE EFFECT OF WATER PRESATURATION OF THE CATALYST

| Run No. | % H <sub>2</sub> S | % SO <sub>2</sub> | % N <sub>2</sub> | % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) | Total Flow (L/min.) | Initial Bed Temp. (°F) | Contact Time (sec.) | Duration of Run (min.) | Catalyst Used                      | ΔT Max. Top (°F) | ΔT Max. Middle (°F) | ΔT Max. Bottom (°F) | Max. Temp. (°F) |
|---------|--------------------|-------------------|------------------|------------------|--------------------|-----------------------|---------------------|------------------------|---------------------|------------------------|------------------------------------|------------------|---------------------|---------------------|-----------------|
| 6       | 6.0                | 3.0               | 80.4             | None             | 10.6               | None                  | 51.2                | 150                    | 2.0                 | 125                    | Regen. H <sub>2</sub> O Sat. F-1   | 60               | 255                 | 275                 | 425             |
| 12      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 105                    | Regen. H <sub>2</sub> O Sat. H-151 | 5                | 25                  | 30                  | 150             |
| 13      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 135                    | Regen. H <sub>2</sub> O Sat. H-151 | 5                | 25                  | 35                  | 155             |
| 14      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 165                    | Regen. Dry H-151                   | 80               | 185                 | 190                 | 310             |
| 15      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 105                    | Regen. H <sub>2</sub> O Sat. H-151 | 5                | 40                  | 85                  | 205             |
| 16      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 130                    | Regen. H <sub>2</sub> O Sat. H-151 | 25               | 35                  | 30                  | 150             |
| 17      | 3.0                | 1.5               | 85.5             | None             | 10.0               | None                  | 51.2                | 120                    | 2.0                 | 130                    | Regen. Dry H-151                   | 110              | 220                 | 200                 | 340             |

EXHIBIT 3-10  
COMPARISON OF 100% AND 97% CONVERSION  
IN THE CLAUS REACTOR

Exit Loss as  
 $\text{SO}_2 = 0.0\%$  (Net  $\text{SO}_2$  Conversion=100%)



Exit Loss as  
 $\text{SO}_2 = 0.3\%$  (Net  $\text{SO}_2$  Conversion = 91%)

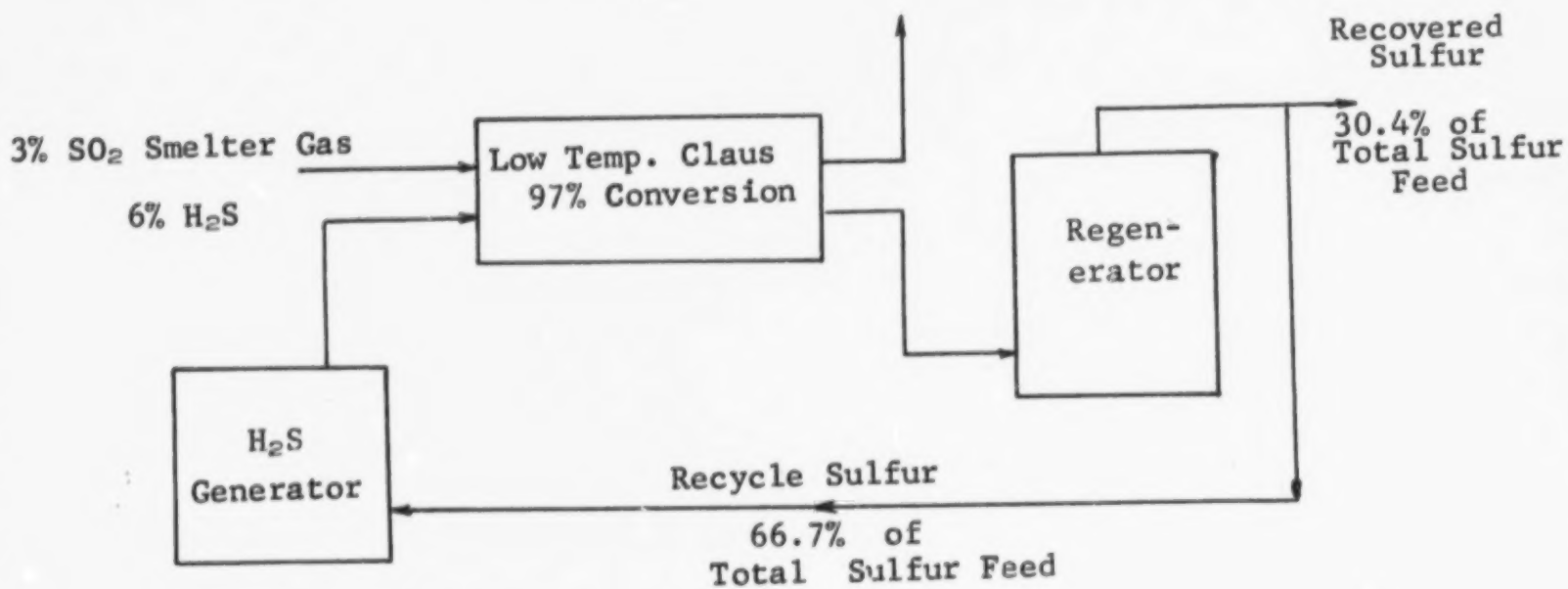




EXHIBIT 3-11

EXPERIMENTAL DETERMINATION OF SULFUR YIELD LOSS  
POUNDS SULFUR/MINUTE  
VS  
MINUTES

$$\frac{\text{Pounds Sulfur Total loss in Exit} \times 100}{\text{Pounds Sulfur Fed}} = \% \text{ Yield Loss}$$

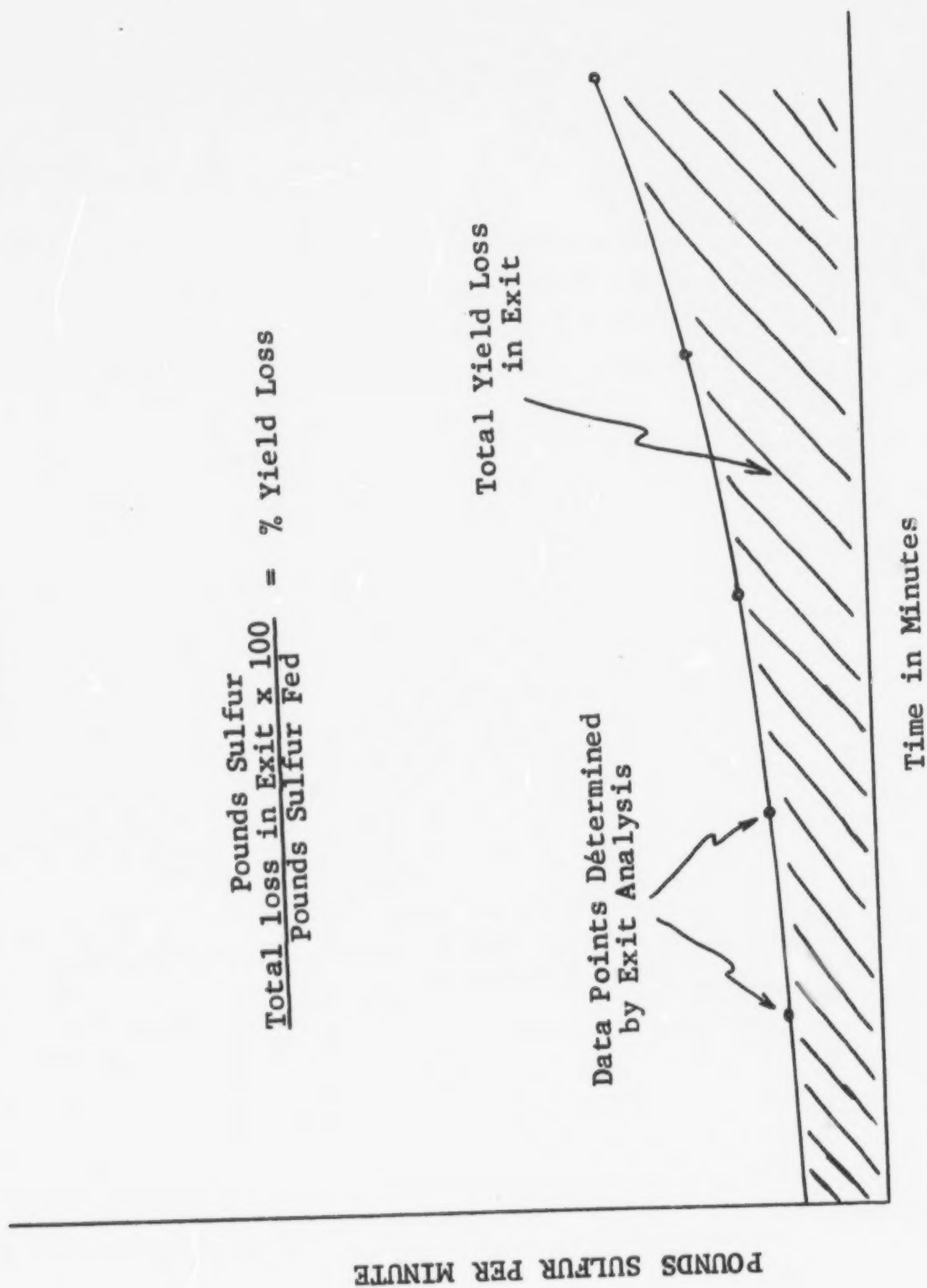


EXHIBIT 3-12

TABULATION DEMONSTRATING H<sub>2</sub>S REACTIONS OVER ACTIVATED ALUMINA

| Run No. | % H <sub>2</sub> S | % SO <sub>2</sub> | % N <sub>2</sub> | % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) | Total Flow (L/min.) | Initial Bed Temp. (°F) | Contact Time (sec.) | Duration of Run (min.) | Catalyst Used | Δ T Max.* Top (°F) | Δ T Max.* Middle (°F) | Δ T Max.* Bottom (°F) | Max. Temp. (°F) |
|---------|--------------------|-------------------|------------------|------------------|--------------------|-----------------------|---------------------|------------------------|---------------------|------------------------|---------------|--------------------|-----------------------|-----------------------|-----------------|
| 29      | 3.5                | None              | 81.5             | 15.0             | None               | None                  | 51.4                | 100                    | 2.0                 | 63                     | Regen. H-151  | 45                 | 60                    | 105                   | 290             |
| 30      | 3.5                | None              | 81.5             | 15.0             | None               | None                  | 51.4                | 255                    | 2.0                 | 158                    | Regen. H-151  | None               | 10                    | 40                    | 295             |
| 31      | 3.0                | None              | 82.0             | 15.0             | None               | None                  | 51.4                | 205                    | 2.0                 | 75                     | Regen. H-151  | 120                | 715                   | 655                   | 920             |
| 28      | 4.0                | None              | 77.0             | 19.0             | None               | None                  | 51.4                | 315                    | 2.0                 | 145                    | Regen. H-151  | 835                | 525                   | 150                   | 1225            |
| 69      | 4.5                | None              | 80.5             | 15.0             | None               | None                  | 51.4                | 75                     | 2.0                 | 85                     | Fresh H-151   | 365                | 800                   | 825                   | 900             |
| 70      | 3.5                | None              | 81.5             | 15.0             | None               | None                  | 51.4                | 150                    | 2.0                 | 85                     | Fresh H-151   | 85                 | 830                   | 645                   | 980             |
| 65      | 6.0                | None              | 79.0             | 15.0             | None               | None                  | 51.4                | 75                     | 2.0                 | 85                     | Fresh F-1     | 25                 | 260                   | 260                   | 335             |
| 66      | 6.0                | None              | 79.0             | 15.0             | None               | None                  | 51.4                | 165                    | 2.0                 | 65                     | Fresh F-1     | 1050+              | 585                   | 600                   | 1200+           |
| 67      | 6.0                | None              | 79.0             | 15.0             | None               | None                  | 51.4                | 250                    | 2.0                 | 75                     | Fresh F-1     | 945+               | 425                   | 415                   | 1200+           |

EXHIBIT 3-13  
COMPARISON OF AVERAGE  
ANALYSIS OF SULFUR BEARING STREAMS

| Run | % H <sub>2</sub> S in | % H <sub>2</sub> S out | % SO <sub>2</sub> out | % S by Difference |
|-----|-----------------------|------------------------|-----------------------|-------------------|
| 29  | 3.40                  | 2.01                   | 0.30                  | 1.09              |
| 30  | 3.47                  | 2.20                   | 0.23                  | 1.04              |
| 31  | 3.32                  | 0.03                   | 2.23                  | 1.06              |
| 28  | 4.09                  | 4.07                   | 0.00                  | 0.02              |
| 69  | 4.50                  | 0.57                   | 2.05                  | 1.88              |
| 70  | 3.80                  | 0.12                   | 2.64                  | 1.04              |
| 65  | 7.07                  | 3.75                   | 0.01                  | 3.31              |
| *66 | 6.38                  | 0.01                   | 14.12                 | -                 |
| *67 | 6.73                  | 0.06                   | 6.84                  | -                 |

\* - Sulfur Initially Present on the Catalyst

EXHIBIT 3-14

TABULATION DEMONSTRATING THE EFFECT OF NO<sub>x</sub>

| Run No. | % H <sub>2</sub> S | % SO <sub>2</sub> | % N <sub>2</sub> | % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) | Total Flow (L/min.) | Initial Bed Temp. (°F) | Contact Time (sec.) | Duration of Run (min.) | Catalyst Used | % Yield Loss | Δ T Max.* Top (°F) | Δ T Max.* Middle (°F) | Δ T Max.* Bottom (°F) | Max. Temp. (°F) |
|---------|--------------------|-------------------|------------------|------------------|--------------------|-----------------------|---------------------|------------------------|---------------------|------------------------|---------------|--------------|--------------------|-----------------------|-----------------------|-----------------|
| 35      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.6                | 120                    | 2                   | 195                    | H-151         | 7.0          | 95                 | 185                   | 185                   | 305             |
| 38      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.6                | 150                    | 2                   | 375                    | H-151         | 17.0         | 85                 | 200                   | 200                   | 350             |
| 45      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.6                | 120                    | 2                   | 282                    | H-151         | 14.0         | 100                | 165                   | 165                   | 285             |
| 36      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | 100                   | 51.6                | 120                    | 2                   | 473                    | H-151         | 28.0         | 85                 | 180                   | 175                   | 300             |
| 37      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | 100                   | 51.6                | 120                    | 2                   | 102                    | H-151         | 17.0         | 105                | 160                   | 160                   | 280             |
| 46      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | 100                   | 51.6                | 120                    | 2                   | 165                    | H-151         | 33.6         | 95                 | 165                   | 175                   | 295             |
| 43      | 1.2                | 0.6               | 73.2             | 15.0             | 10.0               | None                  | 51.6                | 120                    | 2                   | 130                    | H-151         | 17.0         | 95                 | 175                   | 175                   | 295             |
| 44      | 1.2                | 0.6               | 73.2             | 15.0             | 10.0               | 100                   | 51.6                | 120                    | 2                   | 130                    | H-151         | 25.0         | 95                 | 160                   | 160                   | 280             |
| 34      | 3.0                | 1.5               | 70.5             | 15.0             | 10.0               | None                  | 51.6                | 120                    | 2                   | 68                     | H-151         | 19.5         | 115                | 300                   | 300                   | 420             |
| 40      | 3.0                | 1.5               | 80.5             | 15.0             | None               | None                  | 51.6                | 120                    | 2                   | 150                    | H-151         | 17.2         | 45                 | 120                   | 125                   | 275             |
| 32      | 3.0                | 1.5               | 70.5             | 15.0             | 10.0               | 100                   | 51.4                | 120                    | 2                   | 103                    | H-151         | 26.5         | 185                | 520                   | 460                   | 640             |
| 33      | 3.0                | 1.5               | 70.5             | 15.0             | 10.0               | 100                   | 51.4                | 120                    | 2                   | 98                     | H-151         | 25.5         | 215                | 620                   | 550                   | 740             |

EXHIBIT 3-15

TABULATION DEMONSTRATING CATALYST DEGRADATION

| Run No. | % H <sub>2</sub> S | % SO <sub>2</sub> | % N <sub>2</sub> | % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) | Total Flow (L/min.) | Initial Bed Temp. (°F) | Contact Time (sec.) | Duration of Run (min.) | Catalyst Used | % Yield Loss | Δ T Max.* Top (°F) | Δ T Max.* Middle (°F) | Δ T Max.* Bottom (°F) | Max. Temp. (°F) |
|---------|--------------------|-------------------|------------------|------------------|--------------------|-----------------------|---------------------|------------------------|---------------------|------------------------|---------------|--------------|--------------------|-----------------------|-----------------------|-----------------|
| 41      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.4                | 120                    | 2                   | 200                    | H-151         | 0.7          | 120                | 155                   | 135                   | 275             |
| 45      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.4                | 120                    | 2                   | 282                    | H-151         | 14.0         | 100                | 165                   | 165                   | 285             |
| 46      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.4                | 120                    | 2                   | 165                    | H-151         | 33.6         | 95                 | 165                   | 175                   | 295             |
| 47      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.4                | 120                    | 2                   | 98                     | F-1           | None         | 45                 | 135                   | 115                   | 255             |
| 57      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.4                | 120                    | 2                   | 157                    | F-1           | 10.0         | 35                 | 115                   | 105                   | 235             |
| 58      | 0.6                | 0.3               | 74.1             | 15.0             | 10.0               | None                  | 51.4                | 120                    | 2                   | 107                    | F-1           | 8.3          | 35                 | 35                    | 105                   | 225             |



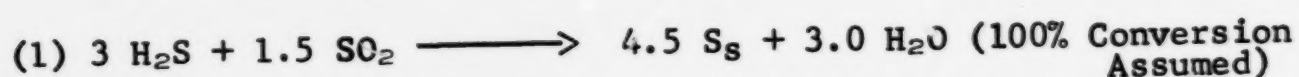
### APPENDIX 3-1

#### CALCULATION OF ADIABATIC TEMPERATURE RISE IN THE H<sub>2</sub>S/SO<sub>2</sub> REACTION

Basis: 100 moles feed at 125°F (approx. 52°C) with the following constituent concentrations

|                  |        |                                                                                                           |
|------------------|--------|-----------------------------------------------------------------------------------------------------------|
| H <sub>2</sub> O | - 10.0 | This assumes a two stage operation<br>with the feed simulating the expected<br>values in the first stage. |
| H <sub>2</sub> S | - 3.0  |                                                                                                           |
| SO <sub>2</sub>  | - 1.5  |                                                                                                           |
| N <sub>2</sub>   | - 86.5 |                                                                                                           |

The following reaction takes place:



$$(\Delta H_{R1})_{25^\circ\text{C}} = (\sum \Delta H_f^\circ) \text{ prod.} - (\sum \Delta H_f^\circ) \text{ react}$$

- where  $\Delta H_f^\circ$  = Heat of formation of products and reactants

$$\begin{aligned} (\Delta H_{R1})_{25^\circ\text{C}} &= 4.5(-.07) + 3.0(-57.80) - 3.0(-4.82) + 1.5(-70.95) \\ &= -52.9 \text{ k cal.} \end{aligned}$$

With the inlet temperature at 125°F and the outlet temperature unknown:

$$(\Delta H_j)_{\text{out}} - (\Delta H_k)_{\text{in}} = (\Delta H_{R1})_{125^\circ\text{F}} \approx (\Delta H_{R1})_{25^\circ\text{C}}$$

- where  $H_j$  and  $H_k$  are enthalpy of the constituents of the inlet and exit gases.

This calculation is conducted in the following manner.

mCp of the feed at 125°F (52°C) is calculated as follows:

| <u>IN</u>        | <u>MOLES</u> | <u>*SPECIFIC HEAT 125°F</u> | <u>nCP</u>          |
|------------------|--------------|-----------------------------|---------------------|
| H <sub>2</sub> O | 10.0         | 8.10                        | 81.0                |
| H <sub>2</sub> S | 3.0          | 8.27                        | 24.8                |
| SO <sub>2</sub>  | 1.5          | 9.92                        | 14.7                |
| N <sub>2</sub>   | 86.5         | 7.00                        | 605.6               |
|                  |              |                             | <u>725.5 cal/°C</u> |

\* Mean C<sub>p</sub> in cal/gm mole/°C  
3-30

### APPENDIX 3-1

$$mCp \Delta T_{in} = 725.5 (52-25) = 19500 \text{ cal.}$$

mCp of the product (assuming final temp. = 248°F) is calculated as follows:

| <u>Out</u>       | <u>Moles</u> | <u>*Specific Heat 248°F</u> | <u>mCp</u>   |
|------------------|--------------|-----------------------------|--------------|
| H <sub>2</sub> O | 13.0         | 8.10                        | 105.2        |
| S <sub>s</sub>   | 4.5          | 6.13                        | 27.6         |
| N <sub>2</sub>   | 86.5         | 7.27                        | 627.0        |
|                  |              |                             | <u>759.8</u> |

The change in temperature then is:

$$\Delta T = \frac{52900 + 19500}{759.8} = 95.4^{\circ}\text{C}$$

and the final temperature is  $95.4^{\circ}\text{C} + 25.0^{\circ}\text{C} = 120.4^{\circ}\text{C}$

$120.4^{\circ}\text{C}$  ( $\approx 249^{\circ}\text{F}$ ) matches the assumed  $248^{\circ}\text{F}$  well,

$$\text{therefore, } \Delta T / \% \text{ SO}_2 = \frac{248^{\circ}\text{F} - 125^{\circ}\text{F}}{1.5\% \text{ SO}_2} = 82^{\circ}\text{F} / \% \text{ SO}_2$$

\* - Mean Cp in cal/gm mole/°C

APPENDIX 3-2  
LOW TEMPERATURE CLAUSE  
COMPILATION OF EXPERIMENTAL DATA

TOP FEED USED  
2 SECOND SUPERFICIAL CONTACT TIME A S.T.P.

| 2. SECOND. SUPERFICIAL CONTROL                            |     |                         |                   |                  |                  |                    |                                |                  |                    |               |                        |                  |                     |                     |                    |              |
|-----------------------------------------------------------|-----|-------------------------|-------------------|------------------|------------------|--------------------|--------------------------------|------------------|--------------------|---------------|------------------------|------------------|---------------------|---------------------|--------------------|--------------|
| Comments                                                  | Run | Nominal Feed Conditions |                   |                  |                  |                    |                                | Responses        |                    |               |                        |                  |                     |                     |                    |              |
|                                                           |     | % H <sub>2</sub> S      | % SO <sub>2</sub> | % N <sub>2</sub> | % O <sub>2</sub> | % H <sub>2</sub> O | NO <sub>x</sub> (ppm) (4 min.) | Total Flow L/min | Initial Temp. (°F) | Catalyst Used | Duration of run (min.) | ΔT max. Top (°F) | ΔT max. Middle (°F) | ΔT max. Bottom (°F) | Maximum Temp. (°F) | % Yield Loss |
| Fresh Catalyst 7.1 sec. contact time for Runs 1, 2, and 3 | 1   | None                    | None              | 89.4             | None             | 10.6               | None                           | 7.2              | 120                | F-1           | 60                     | 150              | -                   | -                   | 270                | -            |
|                                                           | 2   | None                    | None              | 89.4             | None             | 10.6               | None                           | 7.2              | 120                | F-1           | 60                     | 95               | -                   | -                   | 215                | -            |
|                                                           | 3   | None                    | None              | 89.4             | None             | 10.6               | None                           | 7.2              | 120                | F-1           | 300                    | 125              | 115                 | 100                 | 245                | -            |
| Cat Bed Presat with H <sub>2</sub> O                      | 4   | 6.0                     | 3.0               | 73.8             | 10               | 7.2                | None                           | 51.2             | 260                | F-1           | 5                      | 390              | Feed Cut            | 650                 | -                  | -            |
|                                                           | 5   | 6.0                     | 3.0               | 83.8             | None             | 7.2                | None                           | 51.2             | 260                | F-1           | 105                    | 115              | 215                 | 115                 | 480                | -            |
|                                                           | 6   | 6.0                     | 3.0               | 80.4             | None             | 10.6               | None                           | 51.2             | 150                | F-1           | 125                    | 60               | 255                 | 275                 | 425                | -            |
| Cat Bed Presat with H <sub>2</sub> O                      | 7   | 6.0                     | 3.0               | 80.4             | None             | 10.6               | None                           | 51.2             | 150                | F-1           | 110                    | 230              | 275                 | 275                 | 425                | -            |
|                                                           | 8   | None                    | None              | 97.0             | None             | 3.0                | None                           | 51.2             | 120                | H-151         | 100                    | 35               | 115                 | 100                 | 235                | -            |
|                                                           | 9   | None                    | None              | 87.0             | None             | 13.0               | None                           | 51.2             | 120                | H-151         | 100                    | 60               | 115                 | 85                  | 235                | -            |
| Cat Bed Presat with H <sub>2</sub> O                      | 10  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | 120                    | 115              | 160                 | 135                 | 280                | -            |
| Cat Bed Presat with H <sub>2</sub> O                      | 11  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | 75                     | 100              | 190                 | 170                 | 310                | -            |
| Cat Bed Presat with H <sub>2</sub> O                      | 12  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | 105                    | 5                | 25                  | 30                  | 150                | -            |
|                                                           | 13  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | 135                    | 5                | 25                  | 35                  | 155                | -            |
|                                                           | 14  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | 165                    | 80               | 185                 | 190                 | 310                | -            |
| Cat Bed Presat with H <sub>2</sub> O                      | 15  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | 105                    | 5                | 40                  | 85                  | 205                | -            |
| Cat Bed Presat with H <sub>2</sub> O                      | 16  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | 130                    | 25               | 35                  | 30                  | 150                | -            |
|                                                           | 17  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | 130                    | 110              | 220                 | 200                 | 340                | -            |
|                                                           | 18  | 3.0                     | 1.5               | 85.5             | None             | 10.0               | None                           | 51.2             | 120                | H-151         | -                      | -                | -                   | -                   | -                  | -            |
| Oxygen added 20 min. into run                             | 19  | 3.33                    | 1.67              | 95.0             | None             | None               | None                           | 51.4             | 120                | H-151         | 93                     | 60               | 200                 | 200                 | 320                | Some         |
|                                                           | 20  | 3.0                     | 1.5               | 70.5             | 15.0             | 10.0               | Nbae                           | 51.4             | 120                | H-151         | 80                     | 10               | 40                  | 30                  | 360                | Some         |
|                                                           | 21  | 3.0                     | 1.5               | 70.5             | 15.0             | 10.0               | 100                            | 51.4             | 120                | H-151         | 75                     | None             | 30                  | 50                  | 370                | Some         |
|                                                           | 22  | 3.0                     | 1.5               | 70.5             | 15.0             | 10.0               | None                           | 51.4             | 150                | H-151         | 72                     | 10               | 65                  | 90                  | 390                | Some         |
|                                                           | 23  | 3.0                     | 1.5               | 70.5             | 15.0             | 10.0               | 100                            | 51.4             | 150                | H-151         | 60                     | 20               | 135                 | 235                 | 545                | Some         |
|                                                           | 24  | 3.0                     | 1.5               | 70.5             | 15.0             | 10.0               | None                           | 51.4             | 170                | H-151         | 75                     | 15               | 165                 | 265                 | 585                | Some         |
|                                                           | 25  | 3.0                     | 1.5               | 70.5             | 15.0             | 10.0               | None                           | 51.4             | 120                | H-151         | 130                    | 35               | 80                  | 55                  | 455                | 3.5          |
|                                                           | 26  | None                    | None              | 85.0             | 15.0             | None               | None                           | 51.4             | 350                | H-151         | 100                    | None             | None                | None                | 350                | -            |
|                                                           | 27  | 3.0                     | 1.5               | 70.5             | 15.0             | 10.0               | None                           | 51.4             | 120                | H-151         | 127                    | 105              | 185                 | 195                 | 315                | 25.0         |
|                                                           | 28  | 4.0                     | None              | 77.0             | 19.0             | None               | None                           | 51.4             | 390                | H-151         | 145                    | 835              | 525                 | 150                 | 1225               | -            |
|                                                           | 29  | 3.5                     | None              | 81.5             | 15.0             | None               | None                           | 51.4             | 100                | H-151         | 63                     | 45               | 60                  | 105                 | 290                | -            |
|                                                           | 30  | 3.5                     | None              | 81.5             | 15.0             | None               | None                           | 51.4             | 255                | H-151         | 158                    | None             | 10                  | 40                  | 295                | -            |
| 31                                                        | 3.0 | None                    | 82.0              | 15.0             | None             | None               | 51.4                           | 205              | H-151              | 75            | 120                    | 715              | 655                 | 920                 | 26.5               |              |
| 32                                                        | 3.0 | 1.5                     | 70.5              | 15.0             | 10.0             | 100                | 51.4                           | 120              | H-151              | 103           | 185                    | 520              | 460                 | 640                 | 25.5               |              |
| 33                                                        | 3.0 | 1.5                     | 70.5              | 15.0             | 10.0             | 100                | 51.4                           | 120              | H-151              | 98            | 215                    | 620              | 550                 | 740                 | 19.5               |              |
| 34                                                        | 3.0 | 1.5                     | 70.5              | 15.0             | 10.0             | None               | 51.6                           | 120              | H-151              | 68            | 115                    | 300              | 300                 | 420                 | 7.0                |              |
| 35                                                        | 0.6 | 0.3                     | 74.1              | 15.0             | 10.0             | None               | 51.6                           | 120              | H-151              | 95            | 95                     | 185              | 185                 | 305                 | 28.0               |              |
| 36                                                        | 0.6 | 0.3                     | 74.1              | 15.0             | 10.0             | 100                | 51.6                           | 120              | H-151              | 473           | 85                     | 180              | 175                 | 300                 | -                  |              |

4. REDUCTION OF STRONG SO<sub>2</sub> TO SULFUR



4. REDUCTION OF STRONG SO<sub>2</sub> TO SULFUR

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## 4.1 INTRODUCTION

4.1.1 Two major sources of sulfur dioxide contributing to air pollution are the stack gases from fossil fuel-fired power generating stations and from primary non-ferrous smelting operations. The former emits huge volumes of gas with a low (0.20-0.4%)  $\text{SO}_2$  content. In the latter area, copper smelters contribute some 77 percent of the smelter  $\text{SO}_2$  pollution. These gases are variable in both gas composition and in volume. Both sources are very high in oxygen.

4.1.2 It is widely recognized that elemental sulfur is the most desirable final product of  $\text{SO}_2$  pollution abatement processes. This involves reacting the  $\text{SO}_2$  with a reductant such as methane to eventually yield sulfur. Neither of the aforementioned gases are suitable for direct (in-situ) reduction. It has been concluded by Allied Chemical that the most practical approach to the problem is to use a gathering process capable of removing the  $\text{SO}_2$  from the stack gases and delivering to a reduction process a steady flow of essentially 100%  $\text{SO}_2$  on a dry basis. Process and economics developed on using, as an example, the DMA absorption-desorption process coupled with a methane reduction process, bear out this conclusion. The DMA study is given in Section 5 of this report.

4.1.3 Accordingly, work was initiated on an experimental program to define an optimum process profile for reduction of strong  $\text{SO}_2$  with methane. Due to expiration of our contract, only a limited amount of data was generated. The objective of the reported work was to determine the initiation temperature of the  $\text{SO}_2$ - $\text{CH}_4$  reaction, and the temperature-contact time required to approach equilibrium. The primary purpose of determining the initiation temperature was to define the preheat required for the feed gases to the reactor.

## 4.2 SUMMARY

4.2.1 A laboratory investigation was conducted to meet the aforementioned objectives of the study. Twelve runs were made for the strong  $\text{SO}_2$  reduction with  $\text{CH}_4$ . The runs were conducted at conditions of 1000-1500°F at 100°F intervals, 1/2-5 seconds contact time, 0 and 10%  $\text{H}_2\text{O}$  in feed and  $\text{SO}_2/\text{CH}_4$  feed ratio of 2/1. A proprietary catalyst for high temperature primary  $\text{SO}_2$  reduction with  $\text{CH}_4$  was used.

4.2.2 The first part of the study involved investigation of varying temperatures at contact times of 3 and 5 seconds to determine the initiation temperature range. In the other part of the study shorter contact times were investigated at different temperatures to determine the corresponding practical contact time. The synthetic  $\text{SO}_2$  feed gas used simulated a typical product of an  $\text{SO}_2$  gathering plant such as that using the DMA process. For the purpose of evaluating the results obtained, calculations for conversions of  $\text{CH}_4$  and  $\text{SO}_2$  were based only on the exit GC analysis. Near actual contact times were used by assuming a 50% voidage for the catalyst bed.

4.2.3 Preceding this study, theoretical equilibrium calculations on computer were done for strong  $\text{SO}_2$  reduction with  $\text{CH}_4$  by extrapolating from known kinetics developed for weaker  $\text{SO}_2$  reduction with  $\text{CH}_4$  using the same proprietary catalyst. Actual experimentation subsequently followed to verify the validity of the extrapolation.

#### 4.3 CONCLUSIONS AND RECOMMENDATIONS

4.3.1 Preliminary results from the initial portion of the study indicated that at 3 and 5 seconds contact time the minimum reactor temperature or initiation temperature range for the strong  $\text{SO}_2/\text{CH}_4$  reaction was 1400-1500°F. The initiation temperature at 3 seconds contact time was about 1450°F.

4.3.2 At practical contact times such as 1 or 2 seconds, 1450-1500°F appears to be the optimum initiation temperature range. For a reactor temperature of 1500°F and 1 second contact time, conversion of  $\text{CH}_4$  was about 97% and that of  $\text{SO}_2$  was about 83%.

4.3.3 The experimental initiation temperatures obtained were much higher than computer predicted extrapolations from weaker concentration  $\text{SO}_2/\text{CH}_4$  kinetics.

4.3.4 Comparison between feeds with 0%  $\text{H}_2\text{O}$  and 10%  $\text{H}_2\text{O}$  demonstrated no significant difference in both  $\text{CH}_4$  and  $\text{SO}_2$  conversions.

#### 4.4 EXPERIMENTATION AND DISCUSSION

4.4.1 The same apparatus was used in this investigation as in the intermediate reactor studies except for some minor changes such as the use of a different catalyst and the kind and number of feed gases. A diagram of the equipment set-up is found in Exhibit No. 4-1.



4.4.2 The compositions of the feed used in the runs herein reported contain 0% or 10% H<sub>2</sub>O on a wet basis. Introduction of H<sub>2</sub>O in the gaseous mixture was achieved by bubbling the CH<sub>4</sub> component through a water bath maintained at the required temperature. Theoretical feed compositions with 0% and 10% H<sub>2</sub>O are shown in Exhibit No. 4-2.

4.4.3 Actual gas chromatographic analysis of both feed and exit samples are found in Exhibit No. 4-3. The feed analysis is on a dry basis only while the exit is on dry and sulfur-free basis. The "unnormalized" exit analysis should not be directly used in conjunction with the feed to calculate conversions of CH<sub>4</sub> and SO<sub>2</sub> because of volume change due to reaction and different bases (water free, and water and sulfur free). By writing equations for C, H, O and S balance from a general SO<sub>2</sub>/CH<sub>4</sub> reaction equation it can be shown that the exit analysis even on water and sulfur free basis is sufficient to calculate back the actual feed composition (dry basis) and the various conversions. Hence, for the purpose of evaluating the results obtained, calculations were based only on the exit GC analysis. In cases where the calculated inlet feed composition did not agree well with the intended feed composition, the run was either repeated or cancelled if there was an indication of an error in GC analysis or the experimental set up.

4.4.4 From the exit analysis following the above method, CH<sub>4</sub> efficiency, actual SO<sub>2</sub>/CH<sub>4</sub> feed ratio used and conversion of SO<sub>2</sub> to various products have been calculated. Results of these calculations at certain conditions of temperature, contact time and H<sub>2</sub>O content of feed are tabulated for each particular run in Exhibit No. 4-4.

4.4.5 Our arbitrary definition of minimum reactor temperature or initiation temperature for the strong SO<sub>2</sub>/CH<sub>4</sub> reaction is the temperature at which better than 80% SO<sub>2</sub> conversion and better than 90% CH<sub>4</sub> efficiency are achieved at a contact time of 5 seconds or less.

4.4.6 Based on 100 moles of the exit gas, CH<sub>4</sub> efficiency is calculated by using the following equation:

$$\text{CH}_4 \text{ Efficiency} = \frac{(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}}{(\text{CH}_4)_{\text{in}}} \times 100$$

where;  $(\text{CH}_4)_{\text{in}} = (\text{CO}_2 + \text{CO} + \text{CH}_4 + \text{COS} + \text{CS}_2)_{\text{exit}}$

$$(\text{CH}_4)_{\text{out}} = \left[ \left( \frac{\text{CO} + \text{H}_2}{4} \right) + \text{CH}_4 \right]_{\text{exit}}$$

Note: The chemical formulae of the compounds shown in these equations represent the corresponding number of moles of the compound.

The actual  $\text{SO}_2/\text{CH}_4$  feed ratio is computed as follows:

$$(\text{SO}_2/\text{CH}_4)\text{feed ratio} = \frac{(\text{SO}_2)_{\text{in}(\text{calc})}}{(\text{CH}_4)_{\text{in}(\text{calc})}}$$

$$\frac{(\text{SO}_2)_{\text{in calc.}}}{(\text{CH}_4)_{\text{in calc.}}} = \left[ \frac{3/2 (\text{CO} + \text{COS}) + 2 \text{CO}_2 + \text{SO}_2 + \text{CS}_2 - 1/2 (\text{H}_2 + \text{H}_2\text{S})}{(\text{CO}_2 + \text{CO} + \text{CH}_4 + \text{COS} + \text{CS}_2)} \right]_{\text{exit}}$$

4.4.7  $\text{SO}_2$  conversions to various products are calculated from the following:

$$\text{Total } \text{SO}_2 \text{ Conversion} = \frac{(\text{SO}_2)_{\text{in}} - (\text{SO}_2)_{\text{exit}}}{(\text{SO}_2)_{\text{in}}} \times 100$$

$$\text{SO}_2 \text{ Conversion to COS} = \frac{(\text{COS})_{\text{exit}}}{(\text{SO}_2)_{\text{in}}} \times 100 = R_1$$

$$\text{SO}_2 \text{ Conversion to H}_2\text{S} = \frac{(\text{H}_2\text{S})_{\text{exit}}}{(\text{SO}_2)_{\text{in}}} \times 100 = R_2$$

$$\text{SO}_2 \text{ Conversion to CS}_2 = \frac{2(\text{CS}_2)_{\text{exit}}}{(\text{SO}_2)_{\text{in}}} \times 100 = R_3$$

$$\text{Unreacted } \text{SO}_2 = \frac{(\text{SO}_2)_{\text{exit}}}{(\text{SO}_2)_{\text{in}}} \times 100 = R_4$$

$\text{SO}_2$  conversion to sulfur is calculated by difference as follows:

$$\text{SO}_2 \text{ Conversion to S} = 100 - (R_1 + R_2 + R_3 + R_4)$$

4.4.8 The data in Exhibit No. 4-4 indicate that at a temperature of  $1400^\circ\text{F}$ , 3 seconds contact time with 10% water, and 5 seconds contact time with 0% water, and at  $1500^\circ\text{F}$  and 1 second contact time, greater than 95%  $\text{CH}_4$  efficiency is attained. About 60-70%  $\text{SO}_2$  is converted to sulfur and about 10-20%  $\text{SO}_2$  remains unreacted.

4.4.9 A plot of varying temperatures against  $\text{CH}_4$  efficiency and  $\text{SO}_2$  conversion at fixed contact time of 3 seconds and 0%  $\text{H}_2\text{O}$  in feed is shown in Exhibit No. 4-5. This plot indicates that at  $1450^\circ\text{F}$  about 99%  $\text{CH}_4$  efficiency and about 90%  $\text{SO}_2$  conversion should be obtainable at the said conditions. Exhibit No. 4-6 shows a plot of contact time versus  $\text{CH}_4$  efficiency and  $\text{SO}_2$  conversion at  $1500^\circ\text{F}$  and 10%  $\text{H}_2\text{O}$  wherein

about 1 second appears to be the optimum contact time corresponding to a temperature of 1500°F (97% CH<sub>4</sub> efficiency and 83% SO<sub>2</sub> conversion).

4.4.10 A comparison between 0% H<sub>2</sub>O and 10% H<sub>2</sub>O to determine the effect of the presence of H<sub>2</sub>O in the reaction between strong SO<sub>2</sub> and CH<sub>4</sub> is found in Exhibit No. 4-7. The data indicate no significant variation in CH<sub>4</sub> efficiency and total SO<sub>2</sub> conversion between feeds containing 0% H<sub>2</sub>O and 10% H<sub>2</sub>O.

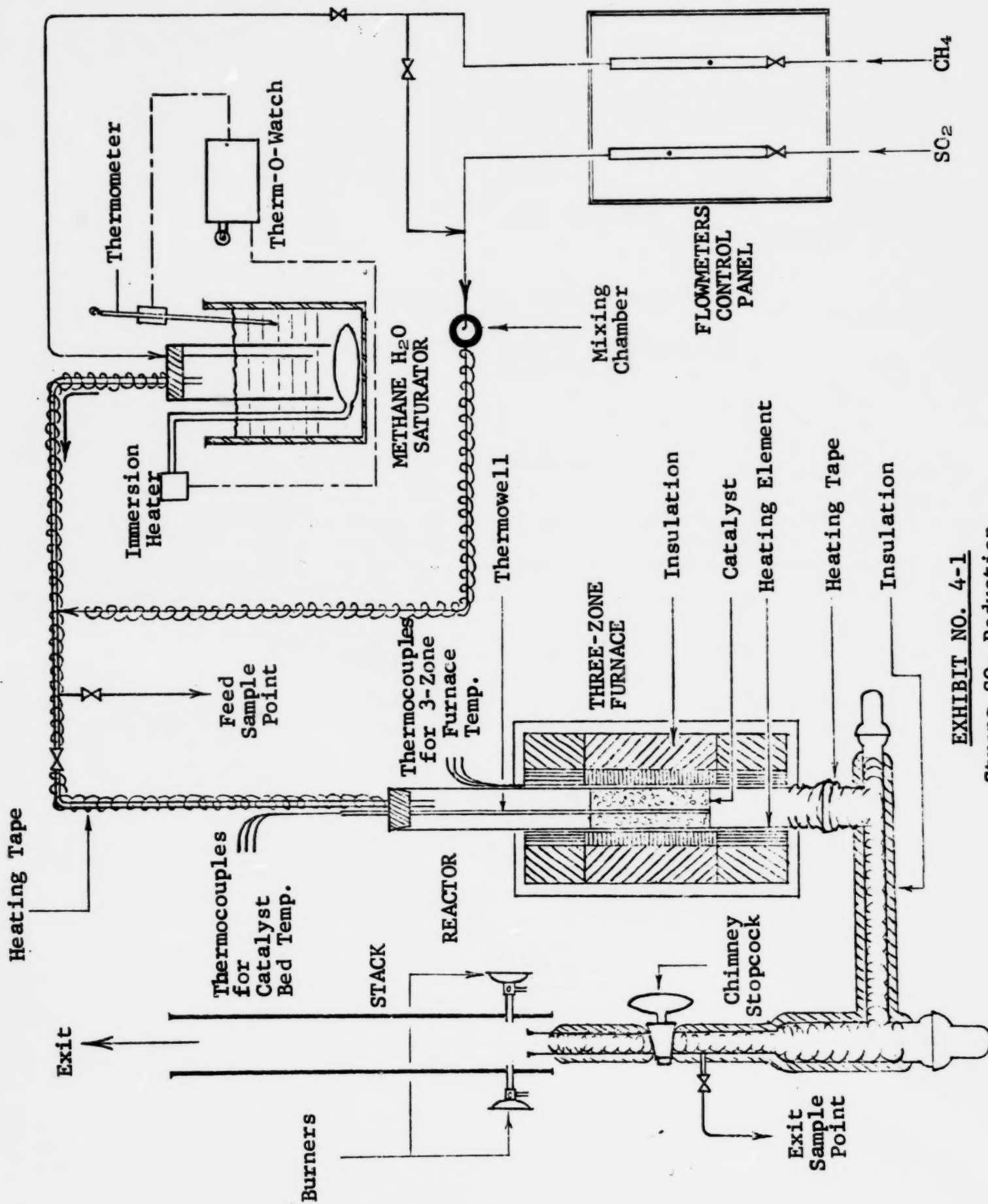


EXHIBIT NO. 4-1  
Strong SO<sub>2</sub> Reduction  
Equipment Set-Up



EXHIBIT NO. 4-2

STRONG SO<sub>2</sub>/CH<sub>4</sub> REDUCTION

Theoretical Feed Compositions  
(Volume %)

0% H<sub>2</sub>O

| Component       | Dry Basis    |
|-----------------|--------------|
| SO <sub>2</sub> | 66.67%       |
| CH <sub>4</sub> | <u>33.33</u> |
| Total           | 100.00%      |

10% H<sub>2</sub>O

| Component        | Wet Basis     | Dry Basis      |
|------------------|---------------|----------------|
| SO <sub>2</sub>  | 60.0%         | 66.67%         |
| CH <sub>4</sub>  | 30.0          | 33.33          |
| H <sub>2</sub> O | 10.0          | -              |
| Total            | <u>100.0%</u> | <u>100.00%</u> |

EXHIBIT NO. 4-3

STRONG SO<sub>2</sub>/CH<sub>4</sub> REDUCTION

Experimental Data

| Run No. | Nominal Temp. °F | Actual Contact Time sec. | H <sub>2</sub> O in Feed % | Gas Composition, Volume % |                |                |                 |    |                 |     |                  |                 |                 |                                          |                |                |                 |      |                 |      |                  |                 |                 |
|---------|------------------|--------------------------|----------------------------|---------------------------|----------------|----------------|-----------------|----|-----------------|-----|------------------|-----------------|-----------------|------------------------------------------|----------------|----------------|-----------------|------|-----------------|------|------------------|-----------------|-----------------|
|         |                  |                          |                            | Feed (Dry Basis)          |                |                |                 |    |                 |     |                  |                 |                 | Unnormalized Exit (Dry and S-Free Basis) |                |                |                 |      |                 |      |                  |                 |                 |
|         |                  |                          |                            | H <sub>2</sub>            | O <sub>2</sub> | N <sub>2</sub> | CH <sub>4</sub> | CO | CO <sub>2</sub> | COS | H <sub>2</sub> S | CS <sub>2</sub> | SO <sub>2</sub> | H <sub>2</sub>                           | O <sub>2</sub> | N <sub>2</sub> | CH <sub>4</sub> | CO   | CO <sub>2</sub> | COS  | H <sub>2</sub> S | CS <sub>2</sub> | SO <sub>2</sub> |
| SSR-1   | 1000             | 3                        | 0                          | ----- NO ANALYSIS -----   |                |                |                 |    |                 |     |                  |                 |                 |                                          |                |                |                 |      |                 |      |                  |                 |                 |
| SSR-2   | 1200             | 3                        | 0                          | 0                         | 0              | 0.19           | 33.80           | 0  | 0.10            | 0   | 0                | 0               | 65.5            | 0                                        | 0.03           | 0.25           | 34.0            | 0    | 0.43            | 0    | 0                | 0               | 65.2            |
| SSR-3   | 1200             | 5                        | 0                          | 0                         | 0              | 0.16           | 34.07           | 0  | 0.17            | 0   | 0                | 0               | 65.6            | 0                                        | 0              | 0.19           | 35.0            | 0.10 | 0.90            | 0.02 | 0.09             | 0               | 63.5            |
| SSR-4   | 1300             | 5                        | 0                          | 0                         | 0              | 0.15           | 32.40           | 0  | 0.12            | 0   | 0                | 0               | 67.3            | 0                                        | 0              | 0.18           | 33.6            | 0.25 | 2.16            | 0.09 | 0.22             | 0               | 63.6            |
| SSR-5   | 1400             | 3                        | 0                          | 0                         | 0.04           | 0.26           | 33.80           | 0  | 0.01            | 0   | 0                | 0               | 66.0            | 0.14                                     | 0.11           | 0.46           | 30.1            | 0.77 | 6.1             | 0.40 | 0.68             | 0.43            | 60.8            |
| SSR-6   | 1400             | 5                        | 0                          | 0                         | 0.05           | 0.36           | 28.80           | 0  | 0               | 0   | 0                | 0               | 70.8            | 0.40                                     | 0.06           | 0.51           | 0.11            | 0.25 | 55.89           | 0.94 | 11.65            | 1.55            | 28.64           |
| SSR-10  | 1400             | 3                        | 10                         | 0                         | 0              | 0.12           | 32.38           | 0  | 0               | 0   | 0                | 0               | 67.5            | 1.43                                     | 0.02           | 0.64           | 1.83            | 0.63 | 47.9            | 1.36 | 21.7             | 5.31            | 19.3            |
| SSR-11  | 1400             | 5                        | 10                         | 0                         | 0.07           | 0.45           | 40.1            | 0  | 0.15            | 0   | 0                | 0               | 59.3            | 1.15                                     | 0.01           | 0.51           | 0.64            | 0.39 | 59.3            | 1.14 | 21.4             | 1.97            | 13.4            |
| SSR-12  | 1500             | 1/2                      | 10                         | 0                         | 0.05           | 0.28           | 33.65           | 0  | 0.11            | 0   | 0                | 0               | 66.0            | 1.41                                     | 0.02           | 0.30           | 22.75           | 1.68 | 19.4            | 0.69 | 5.60             | 2.52            | 45.6            |
| SSR-9   | 1500             | 1                        | 10                         | 0                         | 0              | 0              | 32.45           | 0  | 0               | 0   | 0                | 0               | 67.55           | 1.28                                     | 0.03           | 0.36           | 1.22            | 0.60 | 51.7            | 1.45 | 16.08            | 4.15            | 21.35           |
| SSR-8   | 1500             | 2                        | 10                         | 0                         | 0.03           | 0.22           | 32.8            | 0  | 0               | 0   | 0                | 0               | 66.9            | 0.93                                     | 0.10           | 0.72           | 0.02            | 0.31 | 59.6            | 1.22 | 20.3             | 0.63            | 16.05           |
| SSR-7   | 1500             | 2                        | 0                          | 0                         | 0              | 0.19           | 36.6            | 0  | 0.01            | 0   | 0                | 0               | 63.2            | 0.82                                     | 0.01           | 0.29           | 0.07            | 0.38 | 60.1            | 1.35 | 23.18            | 0.83            | 12.96           |

EXHIBIT NO. 4-4

STRONG SO<sub>2</sub>/CH<sub>4</sub> REDUCTION

CH<sub>4</sub> and SO<sub>2</sub> Conversions at Various  
Temperatures, Contact Times and H<sub>2</sub>O Content in Feed

| Run No. | Nominal Temp. °F | Contact Time Sec. | H <sub>2</sub> O in Feed % | Theor. SO <sub>2</sub> /CH <sub>4</sub> Ratio | CH <sub>4</sub> Efficiency % | Actual SO <sub>2</sub> /CH <sub>4</sub> Feed Ratio | SO <sub>2</sub> Conversion % |        |                     |                    |       | Unre-acted SO <sub>2</sub> % |
|---------|------------------|-------------------|----------------------------|-----------------------------------------------|------------------------------|----------------------------------------------------|------------------------------|--------|---------------------|--------------------|-------|------------------------------|
|         |                  |                   |                            |                                               |                              |                                                    | To S                         | To COS | To H <sub>2</sub> S | To CS <sub>2</sub> | Total |                              |
| SSR-1   | 1000             | 3                 | 0                          | 2/1                                           | 2.76                         | 1.82                                               | 2.79                         | 0.03   | 0.14                | 0                  | 2.96  | 97.04                        |
| SSR-2   | 1200             | 3                 | 0                          | 2/1                                           | 6.75                         | 1.89                                               | 6.45                         | 0.13   | 0.32                | 0                  | 6.91  | 93.09                        |
| SSR-3   | 1200             | 5                 | 0                          | 2/1                                           | 19.77                        | 1.98                                               | 16.10                        | 0.53   | 0.91                | 1.15               | 18.69 | 81.31                        |
| SSR-4   | 1300             | 5                 | 0                          | 2/1                                           | 92.27                        | 1.90                                               | 63.42                        | 2.04   | 11.31               | 9.03               | 85.80 | 14.20                        |
| SSR-5   | 1400             | 3                 | 0                          | 2/1                                           | 99.54                        | 2.34                                               | 67.81                        | 0.68   | 8.46                | 2.25               | 79.21 | 20.79                        |
| SSR-6   | 1400             | 5                 | 0                          | 2/1                                           | 95.89                        | 1.96                                               | 52.62                        | 1.22   | 19.40               | 9.50               | 82.74 | 17.26                        |
| SSR-10  | 1400             | 3                 | 10                         | 2/1                                           | 98.38                        | 1.97                                               | 68.09                        | 0.91   | 17.12               | 3.15               | 89.28 | 10.72                        |
| SSR-11  | 1400             | 5                 | 10                         | 2/1                                           | 49.99                        | 1.85                                               | 34.54                        | 0.79   | 6.44                | 5.80               | 47.57 | 52.43                        |
| SSR-12  | 1500             | 1/2               | 10                         | 2/1                                           | 97.14                        | 2.09                                               | 61.73                        | 1.18   | 13.04               | 6.73               | 82.68 | 17.32                        |
| SSR-9   | 1500             | 1                 | 10                         | 2/1                                           | 99.47                        | 2.06                                               | 69.56                        | 0.96   | 15.91               | 0.99               | 87.42 | 12.58                        |
| SSR-8   | 1500             | 2                 | 10                         | 2/1                                           | 99.41                        | 1.99                                               | 68.58                        | 1.08   | 18.61               | 1.33               | 89.60 | 10.40                        |
| SSR-7   | 1500             | 2                 | 0                          | 2/1                                           |                              |                                                    |                              |        |                     |                    |       |                              |



K&E 10 X 10 TO THE CENTIMETER 46 1512  
18 X 25 CM. MADE IN U.S.A.  
KEUFFEL & ESSER CO.

CH<sub>4</sub> Efficiency - SO<sub>2</sub> Conversion, %

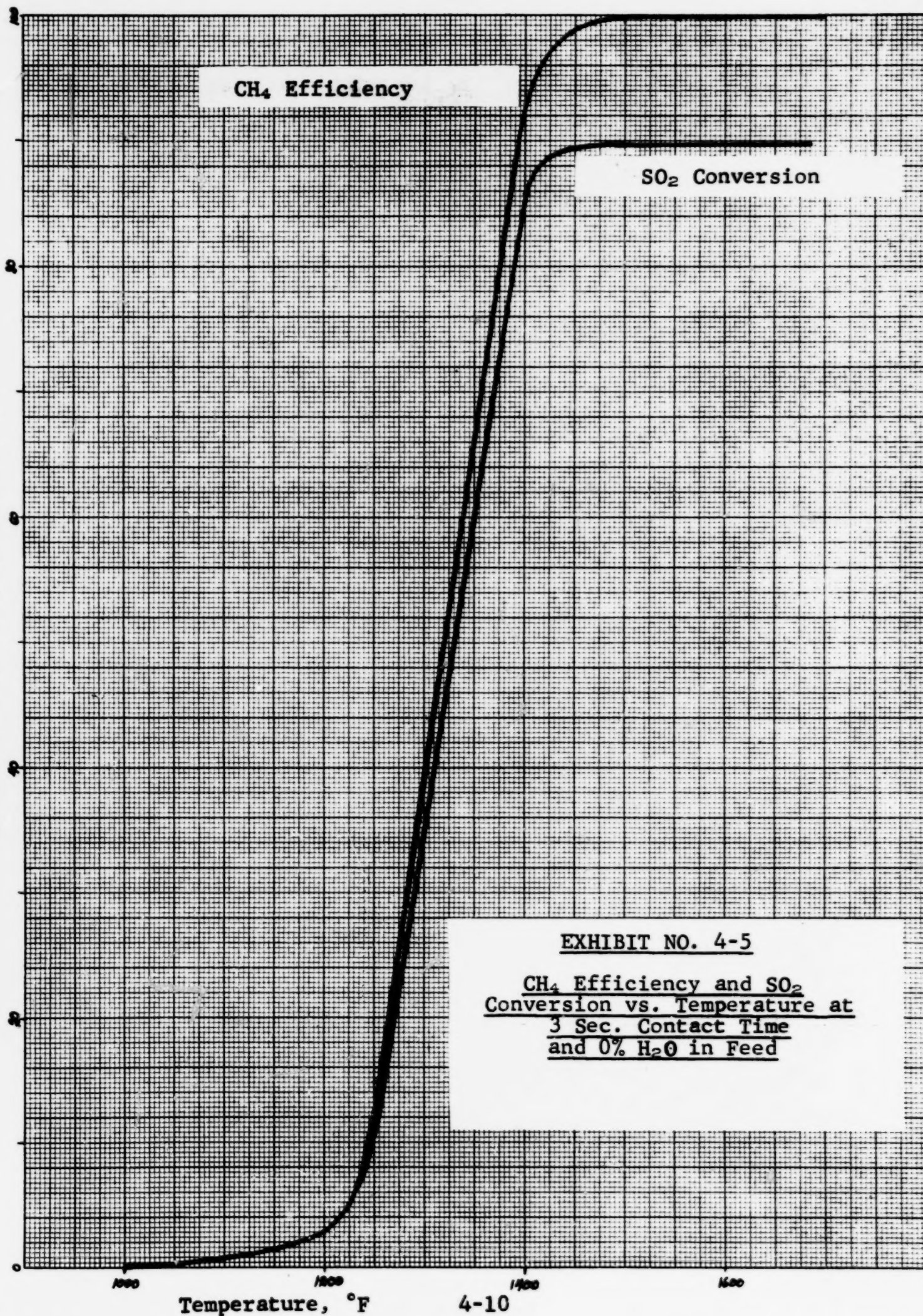


EXHIBIT NO. 4-5

CH<sub>4</sub> Efficiency and SO<sub>2</sub>  
Conversion vs. Temperature at  
3 Sec. Contact Time  
and 0% H<sub>2</sub>O in Feed



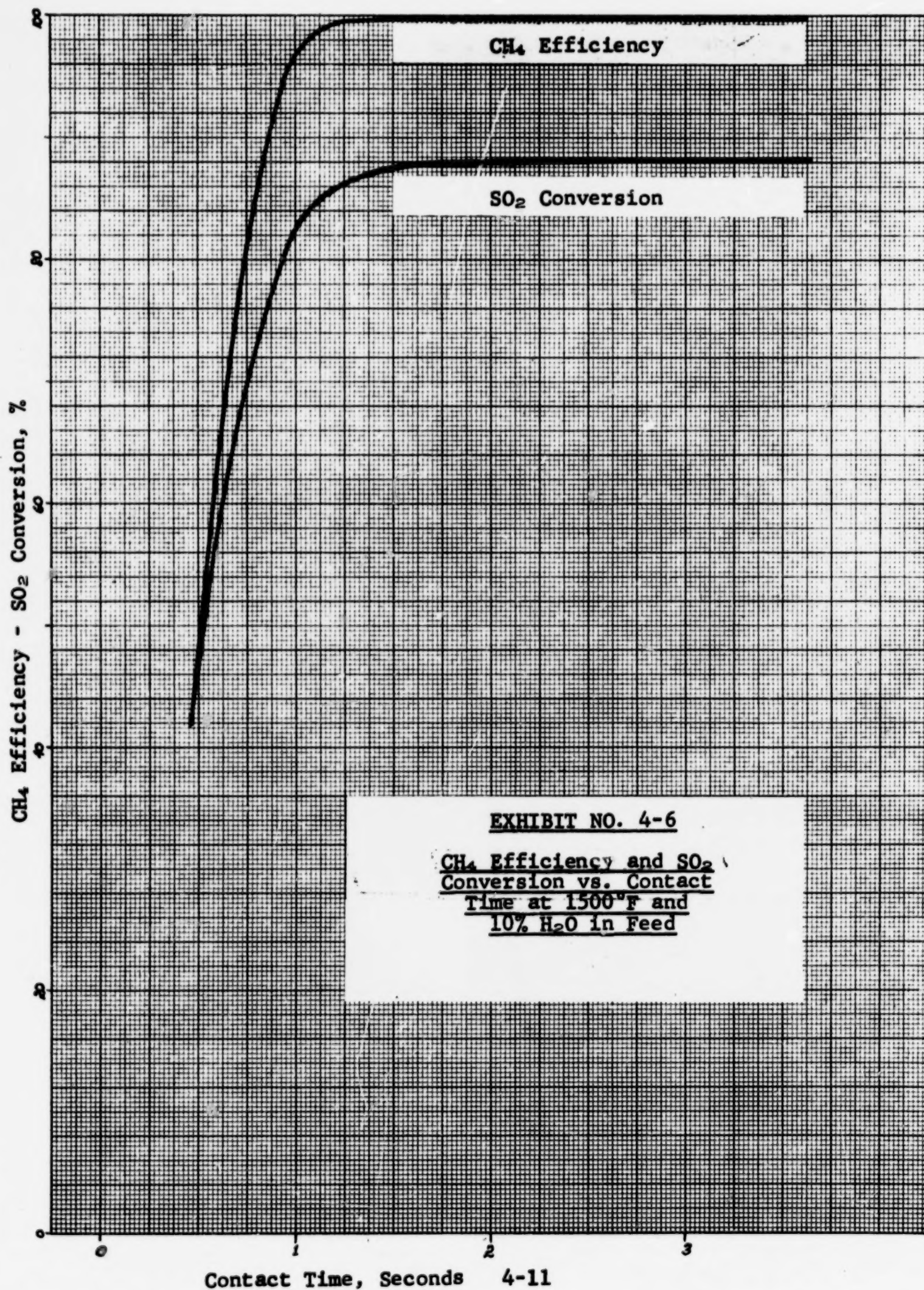


EXHIBIT NO. 4-7

STRONG SO<sub>2</sub>/CH<sub>4</sub> REDUCTION

Comparison Between 0% H<sub>2</sub>O and  
10% H<sub>2</sub>O Data

| Nominal<br>Temp.<br>°F | Contact<br>Time<br>Sec. | H <sub>2</sub> O in<br>Feed<br>% | CH <sub>4</sub><br>Efficiency<br>% | Total SO <sub>2</sub><br>Conversion<br>% |
|------------------------|-------------------------|----------------------------------|------------------------------------|------------------------------------------|
| 1400                   | 3                       | 0                                | 92.27                              | 85.80                                    |
| 1400                   | 3                       | 10                               | 95.89                              | 82.74                                    |
| 1400                   | 5                       | 0                                | 99.54                              | 79.21                                    |
| 1400                   | 5                       | 10                               | 98.38                              | 89.28                                    |
| 1500                   | 2                       | 0                                | 99.41                              | 89.60                                    |
| 1500                   | 2                       | 10                               | 99.47                              | 87.42                                    |

5. STRONG SO<sub>2</sub> FROM SMELTER GAS  
ASARCO DMA PROCESS

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## 5.1 INTRODUCTION

5.1.1 Evaluation of direct reduction to sulfur processes for applicability to  $\text{SO}_2$  pollution abatement in our Phase I studies resulted in several conclusions. Clearly, direct reduction was not applicable to power generating stack gases. In smelter gas studies direct reduction showed acceptable costs only for roaster type gases which are relatively strong in  $\text{SO}_2$  and low in oxygen. However, practically all of the  $\text{SO}_2$  being stacked by smelters is in the form of a weak gas high in oxygen, typically 1-5%  $\text{SO}_2$  and about 15% oxygen. Direct reduction process costs for these gases were excessively high. Based on our knowledge at the time of our Phase I studies, it appeared that only the low temperature Claus (LTC) process would have applicability to low  $\text{SO}_2$ -high oxygen gases. Early in our Phase II laboratory studies on the LTC process, there were indications that assumptions made in our Phase I evaluations were not valid. This pointed out the need for an alternate method of handling smelter  $\text{SO}_2$  emissions.

5.1.2 The low cost of reducing very strong  $\text{SO}_2$  that resulted from some upstream gathering process, using methane as the reductant, suggested that the combined cost of concentrating the  $\text{SO}_2$  and subsequent reduction to sulfur could provide a tenable solution to the smelter pollution problem. On that basis, a survey was made of concentrating schemes that might be employed upstream of the reduction process. The most practical of these appeared to be the dimethylaniline (DMA) sorption process developed by Asarco and used by them in a 20 ton per day  $\text{SO}_2$  plant in Selby, California. Accordingly, the study reported herein is based on use of the Asarco DMA process to scrub smelter exits down to 0.045%  $\text{SO}_2$ , and deliver a 97%  $\text{SO}_2$  gas to the reduction plant.

## 5.2 SUMMARY

5.2.1 Three cases were detailed, based on gases containing 400 NTD of  $\text{SO}_2$  (200 NTD of sulfur), with initial concentrations of 2.9, 4.5 and 8.0 percent  $\text{SO}_2$ .

5.2.2 Factorial extrapolations were made based on costs developed for the 200 NTD sulfur plants to estimate the costs for a 100 and a 400 NTD sulfur plant for each of the gas cases.

5.2.3 These costs were combined with those developed for methane reduction of a 90%  $\text{SO}_2$ -10%  $\text{H}_2\text{O}$  gas in our Phase I studies.

### 5.3 CONCLUSIONS AND RECOMMENDATIONS

5.3.1 A combined system of DMA concentration and high temperature methane reduction of  $\text{SO}_2$  in smelter gas is highly promising. At a production level of 200 NTD of sulfur, using the 4.5%  $\text{SO}_2$  feed case, fixed capital totals out at \$6,400,000 and operating costs at \$33.51 per short ton of sulfur. These costs become lower as plant size increases or feed gas is higher in  $\text{SO}_2$  content.

5.3.2 For the 2.9 to 8.0%  $\text{SO}_2$  range, the combined DMA concentration-high temperature  $\text{CH}_4$  reduction process is clearly better than direct  $\text{CH}_4$  reduction. Both fixed capital and operating costs are lower. This will hold for the 100 to 400 NTD sulfur capacity levels.

5.3.3 The DMA plant is costly due to use of SS 316 throughout as a proven material. There are probably opportunities to reduce capital cost by substitution of reinforced plastics, liners, and the like. The savings in fixed charges could be significant.

5.3.4 In these studies, a steady flow and constant composition to the DMA process were assumed. In the real smelter situation, some modification in the design and operation of the DMA unit will be needed to accomodate the fluctuating gas volume and  $\text{SO}_2$  content.

5.3.5 Work should be done on developing and optimizing a reduction process for 100%  $\text{SO}_2$  that will represent improvements in operability and economics over heretofore visualized processes.

### 5.4 DMA PROCESS STUDY

#### 5.4.1 General

5.4.1.1 Because of the high cost of sulfur recovery by reduction of weak smelter gases (2.9% to 4.5%  $\text{SO}_2$ ), a survey was made of concentrating schemes that might be employed upstream of the reduction process. The most practical of these appears to be the dimethylaniline (DMA) sorption process used by Asarco at their plant in Selby, California (References 1 and 2). This plant and its performance has been reported in sufficient detail to allow a scaleup from its 10 tons per day sulfur equivalent from a 5%  $\text{SO}_2$  feed gas to the 100 to 400 tons/day range reported here.

5.4.1.2 Three cases have been worked up, two based on the 2B and 2C gases defined in the PH 22-68-24 Phase I report and a third gas designated 2D. The gas compositions and the volume equivalent to 400 tons  $\text{SO}_2$ /day are summarized as follows:

Table 5-1

| Gas Designation                   | 2D     | 2B     | 2C      |
|-----------------------------------|--------|--------|---------|
| Volume % SO <sub>2</sub>          | 8.0    | 4.5    | 2.9     |
| Volume % O <sub>2</sub>           | 8.8    | 16.5   | 14.3    |
| Volume % N <sub>2</sub> and Inert | 83.2   | 79.0   | 82.8    |
| SCFM                              | 39,400 | 70,000 | 108,600 |

5.4.1.3 The Selby unit employed lead equipment throughout. More recent practice utilizes stainless steel type 316, therefore stainless is specified herein for lower costs. Exhibit 5-1 is a flow diagram of the process including equipment for cooling and cleaning the input smelter gas.

5.4.1.4 The sizing of the units and the estimation of cooling and heating duties are based on the following data.

Table 5-2  
SO<sub>2</sub> Solubility in DMA

| Gas | Equilibrium (68°F) | Operating |
|-----|--------------------|-----------|
| 2D  | 340 gpl            | 204 gpl   |
| 2B  | 225 gpl            | 135 gpl   |
| 2C  | 150 gpl            | 90 gpl    |

Table 5-3  
Sp. Heat of DMA

|         |       |
|---------|-------|
| 32-68°F | 0.416 |
| 32°F    | 0.403 |
| 68°F    | 0.430 |
| 77°F    | 0.440 |

Heat of solution of SO<sub>2</sub> in DMA at 72°F = 22100 BTU/# mole SO<sub>2</sub>. Sp. gravity of DMA is 0.956 at 68°F.

Table 5-4

Viscosity of DMA

| °F  | Centipoise |
|-----|------------|
| 50  | 1.69       |
| 68  | 1.40       |
| 86  | 1.17       |
| 104 | 1.04       |
| 122 | 0.91       |

Both the density and viscosity of DMA are very close to water, so water ratings are used for DMA pump duty.

5.4.2 Gas Cooler and Cleaner

5.4.2.1 This is a packed tower designed according to Chemical Engineers' Handbook, Perry, Ed. III, pages 680-681. The gas is taken at 500°F and carrying 0.2 grains dust/scf. If the smelter gas is substantially hotter than 500°F we assume it would be dropped to 500°F in a waste heater boiler. The dust loading of 0.2 grains/scf will give a solids content of 0.046% in the water leaving the unit. Water enters the tower at 65°F and discharges at 180°F. The solids are settled out in a pond. The smelter gas is cooled to 68°F.

Table 5-5

Gas Cooler Design Conditions

|                          | Gas | > 2D | 2B   | 2C   |
|--------------------------|-----|------|------|------|
| Cooling water to tower   | gpm | 303  | 530  | 823  |
| Cooling water from tower | gpm | 296  | 517  | 804  |
| Tower diameter - feet    |     | 15.0 | 20.0 | 25.0 |

5.4.2.2 An arbitrary packed depth of 50 feet is used; this may be more than necessary. A packing of 2" dumped rings will have a pressure drop of 0.40" H<sub>2</sub>O/ft or 20" H<sub>2</sub>O on a 50 foot bed. Indicated operating conditions will be safely below the flood point.



### 5.4.3 DMA Absorber - Scrubber

5.4.3.1 This bubble cap absorber is sized according to Perry, Ed. III, page 579 and conditions are as follows:

Liquid Density - 0.98 sp. gr.  
Tray Spacing - 24"  
Liquid Seal - 1.5"  
Superficial Velocity - 4.55 ft/sec

Absorber 8 trays  
Soda Scrubber 2 trays  
Acid Scrubber 9 trays

TOTAL 19 trays

Assume pressure drop of 2.0" water/tray, then total pressure drop = 38"water.

Table 5-6

Absorber Design Conditions

| Gas →                      | 2D     | 2B     | 2C     |
|----------------------------|--------|--------|--------|
| Lbs. pregnant DMA/min.     | 2881.5 | 4159.2 | 6238.8 |
| Lbs. SO <sub>2</sub> /min. | 561.9  | 561.5  | 561.5  |
| Lbs. DMA/min.              | 2319.6 | 3597.7 | 5677.3 |
| Gals. DMA/min.             | 292    | 452    | 713    |
| Absorber Dia. - ft         | 15.3   | 19.5   | 23.9   |
| Absorber Height - ft       | 50.0   | 50.0   | 50.0   |

### 5.4.4 Absorber Intercoolers

5.4.4.1 The intercoolers are numbered on Exhibit 5-1. No detailed information on the tray temperatures in the Selby unit was given. In this design a larger fraction of the SO<sub>2</sub> absorption is taken on the lower plates where the partial pressure of SO<sub>2</sub> is higher. This reduces the heat release on the upper trays where it is important to have a low DMA temperature on trays scrubbing the leanest gas.

Cooling Water - 65°F

U = 100 BTU/hr - sq. ft. - °F

5.4.4.2 Table 5-7 following carries a summary of intercooler parameters.

#### 5.4.5 Intercooler Recirculation Pumps

5.4.5.1 Pumps for the indicated volume of DMA are rated as if DMA were water. Required head is equal to the pressure loss in the exchangers and lines.

#### 5.4.6 Dilute H<sub>2</sub>SO<sub>4</sub> and Dilute Soda Supply

5.4.6.1 The reagent requirements and the supply tank size for a three-day supply of each dilute reagent is as follows. DMA make may be from a small storage tank or from drums.

Table 5-8

| Reagent                                     | 2D    | 2B    | 2C    |
|---------------------------------------------|-------|-------|-------|
| Soda Ash #/day                              | 8000  | 14200 | 22200 |
| H <sub>2</sub> SO <sub>4</sub> (100%) #/day | 9000  | 16000 | 25000 |
| DMA #/day                                   | 250   | 440   | 590   |
| 3 day supply 20% reagent, gal.              | 11000 | 20000 | 30000 |

#### 5.4.7 Smelter Gas Blower

5.4.7.1 Pressure drop of gas cooler is 20" H<sub>2</sub>O, plus the absorber drop of 38" H<sub>2</sub>O gives a total to 58". Horsepower at 60% efficiency is tabulated below.

Table 5-9

|            | 2D    | 2B    | 2C     |
|------------|-------|-------|--------|
| cfm (68°F) | 42300 | 77500 | 120000 |
| Horsepower | 640   | 1170  | 1820   |

#### 5.4.8 Phase Separator and Surge Tanks

5.4.8.1 Based on 15 minutes retention in the phase separation system, the following tank sizes are required.

Table 5-10

|                                    | 2D   | 2B   | 2C    |
|------------------------------------|------|------|-------|
| DMA Surge tank and separator - gal | 5200 | 7500 | 11000 |
| Stripper water surge tank - gal    | 1000 | 1100 | 1200  |

Table 5-7

Intercooler Parameters

| Cooler No.<br>Gas Type         | 1    |      |      | 2    |      |      | 3    |      |      | 4    |      |      | 5    |      |      |
|--------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|                                | 2D   | 2B   | 2C   | 2D   | 2B   | 2C   | 2D   | 2B   | 2C   | 2D   | 2B   | 2C   | 2D   | 2B   | 2C   |
| DMA #/min                      | 2880 | 4160 | 6240 | 2880 | 4160 | 6240 | 2880 | 4160 | 6240 | 2880 | 4160 | 6240 | 2880 | 4160 | 6240 |
| DMA in °F                      | 81   | 77   | 73   | 116  | 102  | 91   | 106  | 94   | 84   | 98   | 87   | 85   | 80   | 77   | 73   |
| DMA out °F                     | 68   | 68   | 68   | 68   | 68   | 68   | 68   | 68   | 68   | 68   | 68   | 68   | 68   | 68   | 68   |
| Water GPM                      | 198  | 394  | 547  | 730  | 745  | 755  | 580  | 570  | 528  | 465  | 417  | 570  | 182  | 394  | 547  |
| Water in °F                    | 65   | 65   | 65   | 65   | 65   | 65   | 65   | 65   | 65   | 65   | 65   | 65   | 65   | 65   | 65   |
| Water out °F                   | 75   | 70   | 68   | 75   | 75   | 75   | 75   | 75   | 75   | 75   | 75   | 75   | 75   | 70   | 68   |
| Log mean $\Delta T$ , °F       | 4.35 | 4.75 | 3.95 | 12.3 | 10.9 | 7.82 | 11.8 | 8.7  | 5.58 | 10.3 | 6.5  | 5.82 | 3.94 | 4.75 | 3.95 |
| BTU/hr x 10 <sup>6</sup>       | 0.99 | 0.99 | 0.82 | 3.66 | 3.74 | 3.78 | 2.89 | 2.85 | 2.64 | 2.28 | 2.09 | 2.80 | 0.92 | 0.99 | 0.82 |
| Exchanger Area ft <sup>2</sup> | 2280 | 2090 | 2080 | 2380 | 3420 | 4720 | 2450 | 3270 | 4720 | 2220 | 3200 | 4820 | 2320 | 2090 | 2080 |

#### 5.4.9 Stripper-Regenerator-Rectifier

5.4.9.1 This unit is sized for a  $\text{SO}_2$  rate of 400 tons/day and is the same for all cases. The unit is based on a 1:1 ratio of steam to  $\text{SO}_2$  leaving the rectifier section. It is assumed that the ratio of steam to  $\text{SO}_2$  is 2:1 in the stripping section. The size (dia.) is based on the stripper duty and is somewhat oversize for the regenerator and rectifier sections.

|             |   |          |
|-------------|---|----------|
| Regenerator | - | 7 trays  |
| Stripper    | - | 14 trays |
| Rectifier   | - | 5 trays  |
| TOTAL       |   | 26 trays |

Design basis for stripper section:

|                         |   |              |
|-------------------------|---|--------------|
| Vapor Volume            | - | 9750 scfm    |
| Vapor Temperature       | - | 210°F        |
| Liquid density at 210°F | - | 0.95 sp. gr. |
| Plate Spacing           | - | 18"          |
| Liquid seal             | - | 1.5"         |
| Superficial Velocity    | - | 3.44 ft/sec. |

Then:

|                       |   |         |
|-----------------------|---|---------|
| Column diameter       | - | 9.1 ft. |
| Overall Column Height | - | 45 ft.  |

#### 5.4.10 $\text{SO}_2$ Product Gas Scrubber - Unit 11

5.4.10.1 The unit serves to remove any traces of DMA from the final  $\text{SO}_2$  product. It may not be necessary on gas being reduced to sulfur but it is necessary where the gas is being converted to pure dry  $\text{SO}_2$  for sale as such. This scrubber is included assuming the recovery of DMA justifies its cost. The unit is 6.0 ft. dia. and may be about 10 ft. packed depth. With 10' of packing, the pressure drop will be about 3.1"  $\text{H}_2\text{O}$  using 1 1/2" dumped rings. Sizing is the same for all three cases.

#### 5.4.11 Stripper Condenser - Unit 7

5.4.11.1 This unit is the same for all three cases. The hot  $\text{SO}_2$ - $\text{H}_2\text{O}$  vapor leaving the  $\text{SO}_2$  rectifier is cooled. The water condensate formed is returned to the top plate of the rectifier.



Table 5-11

Stripper Condenser Design - Unit 7

|                              |                        |
|------------------------------|------------------------|
| Gas in                       | - 179°F                |
| Gas and Water out            | - 85°F                 |
| Cooling H <sub>2</sub> O in  | - 65°F                 |
| Cooling H <sub>2</sub> O out | - 125°F                |
| Log mean $\Delta T$          | - 26.2°F               |
| BTU/hr                       | - $6.1 \times 10^6$    |
| Transfer Surface             | - 4680 ft <sup>2</sup> |
| Cooling Water                | - 205 gpm              |

Table 5-12

DMA Exchanger - Unit 8

|                                                                             | 2D   | 2B   | 2C   |
|-----------------------------------------------------------------------------|------|------|------|
| Pregnant DMA in #/min                                                       | 2880 | 4160 | 6240 |
| Net DMA in #/min                                                            | 2320 | 3600 | 5680 |
| Pregnant DMA in °F                                                          | 68   | 68   | 68   |
| Pregnant DMA out °F                                                         | 178  | 178  | 178  |
| DMA in °F                                                                   | 210  | 210  | 210  |
| DMA out °F                                                                  | 100  | 100  | 100  |
| BTU/hr exchange $\times 10^6$                                               | 7.55 | 11.3 | 17.3 |
| Log mean $\Delta T$ °F                                                      | 32.0 | 32.0 | 32.0 |
| Exchanger area ft <sup>2</sup> , basis U = 100<br>BTU/hr ft <sup>2</sup> °F | 2360 | 3700 | 5420 |

Table 5-13

DMA Cooler - Unit 6

|                                                | 2D   | 2B   | 2C   |
|------------------------------------------------|------|------|------|
| Cooling water in °F                            | 65   | 65   | 65   |
| Cooling water out °F                           | 75   | 75   | 75   |
| Log Mean $\Delta T$ °F                         | 10.5 | 10.5 | 10.5 |
| DMA #/min                                      | 2320 | 3600 | 5680 |
| Water gpm                                      | 390  | 607  | 955  |
| BTU/hr x $10^6$                                | 1.95 | 3.02 | 4.77 |
| Exchanger area ft <sup>2</sup> , basis U = 100 | 1850 | 2880 | 4550 |
| DMA in °F                                      | 100  | 100  | 100  |
| DMA out °F                                     | 68   | 68   | 68   |

5.4.12 Regenerator Reboiler - Unit 10

5.4.13 Stripper Reboiler - Unit 9

5.4.13.1 These units are thermosyphon reboilers operating on a water phase. The stripper reboiler water phase probably will carry a small amount of entrained DMA. Conditions taken are as follows:

Steam side - 100 psig steam at 338°F

Water phase - 220°F

U - 200

$\Delta T$  - 118°F

Gives 42.3 ft<sup>2</sup> for  $10^6$  BTU/hr

Table 5-14

|                               | 2D     |       | 2B     |       | 2C     |       |
|-------------------------------|--------|-------|--------|-------|--------|-------|
|                               | Regen. | Strip | Regen. | Strip | Regen. | Strip |
| BTU/hr x $10^6$               | 11.9   | 13.2  | 12.2   | 14.4  | 12.6   | 16.1  |
| Steam #/min                   | 225    | 250   | 231    | 273   | 240    | 304   |
| Transfer area ft <sup>2</sup> | 500    | 560   | 520    | 610   | 530    | 680   |

Steam Demand - 100 psig

Table 5-15

|                                    | 2D    | 2B    | 2C    |
|------------------------------------|-------|-------|-------|
| Steam - lbs/hr.                    | 28500 | 30240 | 32600 |
| # steam/# SO <sub>2</sub> produced | 0.85  | 0.90  | 0.97  |

5.4.14 65°F Cooling and Process Water

Table 5-16

|                        |     | 2D   | 2B   | 2C   |
|------------------------|-----|------|------|------|
| Gas Cooler and Cleaner | gpm | 296  | 530  | 823  |
| Intercoolers           | gpm | 2155 | 2520 | 2950 |
| DMA Cooler             | gpm | 390  | 607  | 955  |
| Rectifier Condenser    | gpm | 205  | 205  | 205  |
| Total                  | gpm | 3046 | 4612 | 4933 |

5.4.15 SO<sub>2</sub> Yield %

|    |      |
|----|------|
| 2D | 99.4 |
| 2B | 99.0 |
| 2C | 98.4 |

Gas exit - 0.045% SO<sub>2</sub>

5.5 ECONOMIC STUDY

5.5.1 Based on the foregoing process design, plants to recover 400 NTD 97% SO<sub>2</sub> gas from feed gases ranging from 2.9% to 8.0% SO<sub>2</sub> according to the flow sheet Exhibit 5-1 were estimated. The results are summarized in Exhibit 5-2, supported by details in Exhibits 5-3 through 5-8 following.

5.5.2 Factorial extrapolations were made from the 400 NTD SO<sub>2</sub> level (200 NTD equivalent sulfur) to cover the range 100 to 400 NTD sulfur capacity. Fixed capital and operation costs are summarized in Exhibit 5-9 and the complete

economic picture portrayed in the plots marked Exhibit 5-10 (where vol. % SO<sub>2</sub> is the parameter) and Exhibit 5-11 where NTD sulfur equivalent is the parameter.

5.5.3 Besides developing SO<sub>2</sub> concentration costs via the DMA process, a principal purpose of this study was to compare the cost of direct methane reduction of "as is" weak smelter gases with the combined cost of DMA concentration followed by methane reduction.

5.5.4 It was earlier established in our Phase I studies that a 90% SO<sub>2</sub> stream could be reduced with methane for about \$11/NT sulfur (200 NTD sulfur capacity), whereas operation on weak gases incurred costs ranging from \$34 to \$47 per NT sulfur. Tables 5-17, 5-18 and 5-19 were prepared to permit this comparison.

Table 5-17

Basis 200 NTD S Equivalent in Feed

| Gas No. | SO <sub>2</sub> | DMA Process |         | Asarco CH <sub>4</sub> Red'n* |         | Total     |         |
|---------|-----------------|-------------|---------|-------------------------------|---------|-----------|---------|
|         |                 | FC, \$ MM   | OC/NT   | FC, \$ MM                     | OC/NT   | FC, \$ MM | OC/NT   |
| 2D      | 8.0%            | \$3.9       | \$17.02 | \$1.40                        | \$10.94 | \$5.3     | \$27.96 |
| 2B      | 4.5%            | 5.0         | \$22.57 | \$1.40                        | \$10.94 | 6.4       | \$33.51 |
| 2C      | 2.9%            | 6.0         | \$28.02 | \$1.40                        | \$10.94 | 7.4       | \$38.96 |

\* All basis 90% SO<sub>2</sub>, 10% H<sub>2</sub>O Feed.

Table 5-18

Basis 400 NTD S Equivalent in Feed

| Gas No. | SO <sub>2</sub> | DMA Process |         | Asarco CH <sub>4</sub> Red'n |         | Total     |         |
|---------|-----------------|-------------|---------|------------------------------|---------|-----------|---------|
|         |                 | FC, \$ MM   | OC/NT   | FC, \$ MM                    | OC/NT   | FC, \$ MM | OC/NT   |
| 2D      | 8.0%            | \$5.9       | \$12.12 | \$2.10                       | \$ 8.59 | 8.0       | \$20.71 |
| 2B      | 4.5%            | 7.6         | \$16.39 | \$2.10                       | \$ 8.59 | 9.7       | \$24.98 |
| 2C      | 2.9%            | 9.0         | \$20.56 | \$2.10                       | \$ 8.59 | 11.1      | \$29.15 |

Table 5-19

Other Methods

| Gas No. | SO <sub>2</sub> | Process                          | FC, \$ MM | OC/NT   | NTD S in Feed |
|---------|-----------------|----------------------------------|-----------|---------|---------------|
| 2B      | 4.5%            | Asarco Type CH <sub>4</sub> Red. | \$9.15    | \$46.83 | 200           |
| 2D      | 8.0%            | No Data                          | -         | -       | -             |



## 5.6 REFERENCES

1. Kohl and Riesenfeld, "Gas Purification", pages 204 through 209.
2. Ind. Eng. Chem. 42, No. 11, pages 2253-2258, "Liquid SO<sub>2</sub> from Waste Smelter Gases", E. P. Fleming & T. C. Fitt.

## STRONG SO<sub>2</sub> FROM SMELTER GAS DNA PROCESS

**400 Tons SO<sub>2</sub> per Day**



## EXHIBIT 5-2

### DMA Economics Summary

"Order of Magnitude" estimates of capital cost to produce 400 NTD SO<sub>2</sub> gas (200 NTD sulfur equivalent) at 97.1 vol.% purity were prepared; supporting details are given in Exhibits 5-3, 5-4 and 5-5 following. The results are summarized below.

Table 5-20

| Case | Smelter Gas Feed Composition |                  |                           | Purchased Equipment | Battery Limits*<br>Fixed Capital |
|------|------------------------------|------------------|---------------------------|---------------------|----------------------------------|
|      | % SO <sub>2</sub>            | % O <sub>2</sub> | % N <sub>2</sub> + Inerts |                     |                                  |
| 2D   | 8.0                          | 8.8              | 83.2                      | \$ 900,000          | \$ 3,900,000                     |
| 2B   | 4.5                          | 16.5             | 79.0                      | \$1,352,000         | \$ 5,000,000                     |
| 2C   | 2.9                          | 14.3             | 82.8                      | \$1,825,000         | \$ 6,000,000                     |

\* The Battery Limits capital excludes nickel surcharge on all stainless steel equipment, includes approximately 25% contingency. No buildings, site preparation, service facilities or effluent control facilities have been included. It is assumed that all utilities at appropriate conditions are available at the battery limits. Piping, instrumentation, electrical gear and overheads were factored into the totals basis purchased equipment cost.

Utility requirements are tabulated below.

Table 5-21

|                                           | Per NT SO <sub>2</sub> Product |                |                |
|-------------------------------------------|--------------------------------|----------------|----------------|
|                                           | <u>Case 2D</u>                 | <u>Case 2B</u> | <u>Case 2C</u> |
| Steam, M lbs                              | 1.70                           | 1.80           | 1.94           |
| Process & Cooling Water, M gals           | 11.0                           | 16.7           | 17.8           |
| Electricity, KWH                          | 33.5                           | 59.1           | 92.9           |
| Feed Gas, SCFM at 400 NTD SO <sub>2</sub> | 39,400                         | 70,000         | 108,600        |

EXHIBIT 5-3

Recovery of 97% SO<sub>2</sub> Vapor From  
4.5% SO<sub>2</sub> Bearing Smelter Gases  
DMA Process - Case 2B  
Summation of Major Equipment

1. Gas Cooler and Cleaner - Tower of 316 stainless steel, scrubbing and cooling smelter gas from 500°F to 68°F. 20 ft. diameter with 50 ft. depth of ceramic packing ----- \$340,000
2. DMA Absorber Scrubber - Bubble cap tower of 316 stainless steel 19 ft.-6 in. diameter by 50 ft. height with 8 absorbing trays, 2 soda scrubbing trays and 9 acid scrubbing trays ----- \$430,000
3. Absorber Intercoolers - Each a 316 stainless steel exchanger.

|    |              |       |           |
|----|--------------|-------|-----------|
| #1 | 2090 sq. ft. | ----- | \$ 20,200 |
| #2 | 3420 sq. ft. | ----- | \$ 33,300 |
| #3 | 3270 sq. ft. | ----- | \$ 31,000 |
| #4 | 3200 sq. ft. | ----- | \$ 31,000 |
| #5 | 2090 sq. ft. | ----- | \$ 20,200 |
4. Recirculating Pumps - Five centrifugal pumps, each of 316 stainless steel, delivering 520 gpm at 40 ft. TDH with 10 HP TEFC motor. Total for five (5) ----- \$ 8,000
5. Dilute Acid Supply Tank - a 20,000 gal. tank of 316 stainless steel ----- \$ 22,000
6. Dilute Soda Supply Tank - a 20,000 gal. tank of 316 stainless steel ----- \$ 22,000
7. DMA Supply Tank - a 200 gal. tank of carbon steel - \$ 400
8. Smelter Gas Blower - To deliver 77,500 cfm at 68°F against 58 in. water, made of 316 stainless steel ----- \$ 46,400  
Drip-proof motor, 1200 HP ----- \$ 18,400
9. Phase Separator - A 7,500 gal. tank of 316 stainless steel ----- \$ 11,900
10. DMA Surge Tank - A 7,500 gal. tank of 316 stainless steel ----- \$ 11,900
11. Separator Tank - A 7,500 gal. tank of 316 stainless steel ----- \$ 11,900
12. Stripper Water Surge Tank - A 1,100 gal. tank of 316 stainless steel ----- \$ 2,100



13. Stripper Regenerator Rectifier - Bubble cap tower of 316 stainless steel 9 ft. diameter by 45 ft. height with 7 regenerating trays, 14 stripping trays, and 5 rectifying trays ----- \$ 135,000
14. SO<sub>2</sub> Product Gas Scrubber - Tower of 316 stainless steel 6 ft. diameter with 10 ft. of ceramic packing --- \$ 23,000
15. Stripper Condenser - A 316 stainless steel exchanger with 4680 sq. ft. transfer area ----- \$ 45,200
16. DMA Exchanger - A 316 stainless steel exchanger with 3700 sq. ft. transfer area ----- \$ 36,000
17. DMA Cooler - A 316 stainless steel exchanger with 2880 sq. ft. transfer area ----- \$ 27,400
18. Regenerator Reboiler - A 316 stainless steel unit with 520 sq. ft. transfer area and up to 100 psig steam on the shell side ----- \$ 6,600
19. Stripper Reboiler - A 316 stainless steel unit with 610 sq. ft. transfer area ----- \$ 7,400
20. Collecting Tank - A 200 gal. tank of 316 stainless steel ----- \$ 1,200
21. Gas Cooler Pump - A 316 stainless steel centrifugal pump to deliver 700 gpm at 100 ft. TDH with 30 HP TEFC motor ----- \$ 2,200
22. 20% Acid Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
23. 20% Soda Pump - 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
24. Stripper Feed Pump - A 316 stainless steel centrifugal pump to deliver 500 gpm at 100 ft. TDH with a 30 HP TEFC motor ----- \$ 1,900
25. DMA Makeup Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
26. Separator feed Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700

27. Recycle Pump - A 316 stainless steel centrifugal pump  
to deliver 500 gpm at 100 ft. TDH with a 30 HP  
TEFC motor ----- \$ 1,900
28. Stripper Bottoms Pump - A 316 stainless steel  
centrifugal pump to deliver 20 gpm at 30 ft. TDH with  
a 2 HP TEFC motor -----\$ 700

TOTAL PURCHASED  
EQUIPMENT \$1,352,000

EXHIBIT 5-4

Recovery of 97% SO<sub>2</sub> Vapor From  
2.9% SO<sub>2</sub> Bearing Smelter Gases  
DMA Process - Case 2C  
Summation of Major Equipment

1. Gas Cooler and Cleaner - Tower of 316 stainless steel, scrubbing and cooling smelter gas from 500°F to 68°F 25 ft. diameter with 50 ft. depth of ceramic packing ----- \$ 478,000
2. DMA Absorber-Scrubber - Bubble cap tower of 316 stainless steel 24 ft. 6 in. diameter by 50 ft. height with 8 absorbing trays, 2 soda scrubbing trays and 9 acid scrubbing trays ----- \$ 614,000
3. Absorber Intercoolers - Each a 316 stainless steel exchanger.  

|    |              |       |    |        |
|----|--------------|-------|----|--------|
| #1 | 2080 sq. ft. | ----- | \$ | 20,100 |
| #2 | 4720 sq. ft. | ----- | \$ | 45,600 |
| #3 | 4720 sq. ft. | ----- | \$ | 45,600 |
| #4 | 4820 sq. ft. | ----- | \$ | 46,500 |
| #5 | 2080 sq. ft. | ----- | \$ | 20,100 |
4. Recirculating Pumps - Five centrifugal pumps, each of 316 stainless steel, delivering 800 gpm at 40 ft. TDH with 15 HP TEFC motor. Total for five (5) ----- \$ 10,800
5. Dilute Acid Supply Tank - A 30,000 gal. tank of 316 stainless steel ----- \$ 26,400
6. Dilute Soda Supply Tank - A 30,000 gal. tank of 316 stainless steel ----- \$ 26,400
7. DMA Supply Tank - A 200 gal. tank of carbon steel - \$ 400
8. Smelter Gas Blower - To deliver 120,000 cfm at 68°F against 58 in. water, made of 316 stainless steel- \$ 95,100  
Drip-proof Motor, 1800 HP ----- \$ 25,300
9. Phase Separator - An 11,000 gal. tank of 316 stainless steel ----- \$ 14,800
10. DMA Surge Tank - An 11,000 gal. tank of 316 stainless steel ----- \$ 14,800
11. Separator Tank - An 11,000 gal. tank of 316 stainless steel ----- \$ 14,800
12. Stripper Water Surge Tank - A 1,200 gal. tank of 316 stainless steel ----- \$ 2,300

13. Stripper Regenerator Rectifier - Bubble cap tower of 316 stainless steel 9 ft. diameter by 45 ft. height with 7 regenerating trays, 14 stripping trays, and 5 rectifying trays ----- \$ 135,000
14. SO<sub>2</sub> Product Gas Scrubber - Tower of 316 stainless steel 6 ft. diameter with 10 ft. of ceramic packing ----- \$ 23,000
15. Stripper Condenser - A 316 stainless steel exchanger with 4680 sq. ft. transfer area ----- \$ 45,000
16. DMA Exchanger - A 316 stainless steel exchanger with 5420 sq. ft. transfer area ----- \$ 50,000
17. DMA Cooler - A 316 stainless steel exchanger with 4550 sq. ft. transfer area ----- \$ 43,900
18. Regenerator Reboiler - A 316 stainless steel unit with 530 sq. ft. transfer area and up to 100 psig steam on the shell side ----- \$ 6,700
19. Stripper Reboiler - A 316 stainless steel unit with 680 sq. ft. transfer area ----- \$ 8,200
20. Collecting Tank - A 200 gal. tank of 316 stainless steel ----- \$ 1,200
21. Gas Cooler Pump - A 316 stainless steel centrifugal pump to deliver 1100 gpm at 100 ft. TDH with 50 HP TEFC motor ----- \$ 2,800
22. 20% Acid Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
23. 20% Soda Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
24. Stripper Feed Pump - A 316 stainless steel centrifugal pump to deliver 750 gpm at 100 ft. TDH with a 40 HP TEFC motor ----- \$ 2,500
25. DMA Makeup Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
26. Separator Feed Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700



27. Recycle Pump - A 316 stainless steel centrifugal pump to  
deliver 750 gpm at 100 ft. TDH with a 40 HP TEFC  
motor ----- \$ 2,500

28. Stripper Bottoms Pump - A 316 stainless steel centrifugal  
pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC  
motor ----- \$ 700

TOTAL PURCHASED EQUIPMENT \$1,825,500

## EXHIBIT 5-5

Recovery of 97% SO<sub>2</sub> Vapor From  
8.0% SO<sub>2</sub> Bearing Smelter Gases  
DMA Process - Case 2D  
Summation of Major Equipment

1. Gas Cooler and Cleaner - Tower of 316 stainless steel, scrubbing and cooling smelter gas from 500°F to 68°F. 15 ft. diameter with 50 ft. depth of ceramic packing ----- \$ 193,000
2. DMA Absorber-Scrubber - Bubble cap tower of 316 stainless steel 15 ft. 4 in. diameter by 50 ft. height with 8 absorbing trays, 2 soda scrubbing trays and 9 acid scrubbing trays ----- \$ 201,600
3. Absorber Intercoolers - Each a 316 stainless steel exchanger
  - #1 2280 sq. ft. ----- \$ 22,100
  - #2 2980 sq. ft. ----- \$ 28,300
  - #3 2450 sq. ft. ----- \$ 23,300
  - #4 2200 sq. ft. ----- \$ 21,300
  - #5 2320 sq. ft. ----- \$ 22,400
4. Recirculating Pumps - Five centrifugal pumps, each of 316 stainless steel, delivering 360 gpm at 40 ft. TDH with 7.5 HP TEFC motor ----- \$ 8,000
5. Dilute Acid Supply Tank - A 11,000 gal. tank of 316 stainless steel ----- \$ 14,800
6. Dilute Soda Supply Tank - A 11,000 gal. tank of 316 stainless steel ----- \$ 14,800
7. DMA Supply Tank - A 200 gal. tank of carbon steel- \$ 400
8. Smelter Gas Blower - To deliver 42,300 cfm at 68°F against 58 in. water, made of 316 stainless steel- \$ 42,800  
Drip-proof motor, 600 HP ----- \$ 9,300
9. Phase Separator - A 5,200 gal. tank of 316 stainless steel ----- \$ 9,700
10. DMA Surge Tank - A 5,200 gal. tank of 316 stainless steel ----- \$ 9,700
11. Separator Tank - A 5,200 gal. tank of 316 stainless steel ----- \$ 9,700

12. Stripper Water Surge Tank - A 1,000 gal. tank of 316 stainless steel ----- \$ 2,100
13. Stripper Regenerator Rectifier - Bubble cap tower of 316 stainless steel, 9 ft. diameter by 45 ft. height with 7 regenerating trays, 14 stripping trays, and 5 rectifying trays ----- \$ 135,000
14. SO<sub>2</sub> Product Gas Scrubber - Tower of 316 stainless steel 6 ft. diameter with 10 ft. of ceramic packing ---- \$ 23,000
15. Stripper Condenser - A 316 stainless steel exchanger with 4680 sq. ft. transfer area ----- \$ 45,200
16. DMA Exchanger - A 316 stainless steel exchanger with 2360 sq. ft. transfer area ----- \$ 22,800
17. DMA Cooler - A 316 stainless steel exchanger with 1850 sq. ft. transfer area ----- \$ 17,900
18. Regenerator Reboiler - A 316 stainless steel unit with 500 sq. ft. transfer area and up to 100 psig steam on the shell side ----- \$ 6,300
19. Stripper Reboiler - A 316 stainless steel unit with 560 sq. ft. transfer area ----- \$ 7,050
20. Collecting Tank - A 200 gal. tank of 316 stainless steel ----- \$ 1,200
21. Gas Cooler Pump - A 316 stainless steel centrifugal pump to deliver 400 gpm at 100 ft. TDH with 20 HP TEFC motor ----- \$ 1,750
22. 20% Acid Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
23. 20% Soda Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
24. Stripper Feed Pump - A 316 stainless steel centrifugal pump to deliver 350 gpm at 100 ft. TDH with a 20 HP TEFC motor ----- \$ 1,350
25. DMA Makeup Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700
26. Separator Feed Pump - A 316 stainless steel centrifugal pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC motor ----- \$ 700

27. Recycle Pump - A 316 stainless steel centrifugal pump  
to deliver 350 gpm at 100 ft. TDH with a 20 HP  
TEFC motor ----- \$ 1,350
28. Stripper Bottoms Pump - A 316 stainless steel centrifugal  
pump to deliver 20 gpm at 30 ft. TDH with a 2 HP TEFC  
motor ----- \$ 700

TOTAL PURCHASED EQUIPMENT \$ 900,000



OPERATING COSTS

PROCESS: DMA Sorption

CASE NO. 2B

Fixed Capital, Battery Limits Basis

\$5,000,000

Sulfur Production

NTD x 330 Days =

66,000 NTY

| Line No. | Cost Items                            | Used Per NT | Cost Per Unit | Per NT Sulfur | Per Year \$M |
|----------|---------------------------------------|-------------|---------------|---------------|--------------|
|          | DMA                                   | 2.2 lbs     | 0.20          | \$ .44        | \$ 29.0      |
|          | Soda Ash                              | 0.036 NT    | \$40.         | 1.44          | 95.0         |
|          | H <sub>2</sub> SO <sub>4</sub> , 100% | 0.04 NT     | \$30.         | 1.20          | 79.0         |
| 1.       | Total Raw Materials                   | -           | -             | \$3.08        | \$ 203.0     |
| 2.       | Direct Labor                          | 8750 MH     | \$3.50        | .47           | 31.0         |
| 3.       | Supervision                           | -           | \$10,000      | .08           | 5.0          |
| 4.       | Maintenance                           | 5% FC       | -             | 3.79          | 250.0        |
| 5.       | Plant Supplies                        | 10%(L2+L3)  | -             | .05           | 3.6          |
| 6. a)    | Electricity                           | 118 KWH     | \$.01         | 1.18          | 78.0         |
| b)       | Cooling Water                         | 33.4 MG     | .05           | 1.68          | 111.0        |
| c)       | Boiler Feed Water                     | - MG        | .25           | -             | -            |
| d)       | Fuel Gas                              | - MCF       | .30           | -             | -            |
| e)       | Steam                                 | 3.6 M lb    | .50           | 1.80          | 118.8        |
| 7.       | Total Utilities                       | -           | -             | 4.66          | 307.8        |
| 8.       | Other Direct (Catalyst)               | -           | -             | -             | -            |
| 9.       | <u>TOTAL DIRECT</u>                   | -           | -             | \$12.13       | \$ 800.5     |
| 10.      | Payroll Burden                        | 30% L2      | -             | .14           | 9.3          |
| 11.      | Plant Overhead                        | 70%(L2+L3)  | -             | .38           | 25.2         |
| 12.      | Pack & Ship                           | -           | -             | -             | -            |
| 13.      | Waste Disposal                        | 1000 MH     | 3.90          | .06           | 3.9          |
| 14.      | Other Indirect                        | -           | -             | -             | -            |
| 15.      | <u>TOTAL INDIRECT</u>                 | -           | -             | \$ .58        | \$ 38.4      |
| 16.      | Depreciation                          | 10% FC      | -             | 7.58          | 500.0        |
| 17.      | Taxes                                 | 2% FC       | -             | 1.52          | 100.0        |
| 18.      | Insurance                             | 1% FC       | -             | .76           | 50.0         |
| 19.      | Other Fixed                           | -           | -             | -             | -            |
| 20.      | <u>TOTAL FIXED</u>                    | -           | -             | \$ 9.86       | \$ 650.0     |
| 21.      | <u>TOTAL OPERATING</u>                | -           | -             | \$22.57       | \$1,488.9    |
| 22.      | Credits                               | -           | -             | -             | -            |
| 23.      | <u>NET OPERATING</u>                  | -           | -             | \$22.57       | \$1,489.     |

OPERATING COSTS

PROCESS: DMA Sorption CASE NO. 2C

Fixed Capital, Battery Limits Basis \$6,000,000  
 Sulfur Production NTD x 330 Days = 66,000 NTY

| Line No. | Cost Items                          | Used Per NT | Cost Per Unit | Per NT Sulfur  | Per Year \$M      |
|----------|-------------------------------------|-------------|---------------|----------------|-------------------|
|          | DMA                                 | 2.95 lbs    | \$ .20        | \$ .59         | \$ 39.0           |
|          | Soda Ash                            | 0.06 NT     | \$ 40.        | 2.40           | 158.5             |
|          | H <sub>2</sub> SO <sub>4</sub> 100% | 0.063 NT    | \$ 30.        | 1.89           | 125.0             |
| 1.       | Total Raw Materials                 | -           | -             | \$ 4.88        | \$ 322.5          |
| 2.       | Direct Labor                        | 8750 MH     | \$3.50        | .47            | 31.0              |
| 3.       | Supervision                         | -           | \$10,000      | .08            | 5.0               |
| 4.       | Maintenance                         | 5% FC       | -             | 4.55           | 300.0             |
| 5.       | Plant Supplies                      | 10%(L2+L3)  | -             | .05            | 3.6               |
| 6. a)    | Electricity                         | 186 KWH     | \$ .01        | 1.86           | 122.5             |
| b)       | Cooling Water                       | 35.6 MG     | .05           | 1.78           | 117.0             |
| c)       | Boiler Feed Water                   | - MG        | .25           | -              | -                 |
| d)       | Fuel Gas                            | MCF         | .30           | -              | -                 |
| e)       | Steam                               | 3.88 M lb   | .50           | 1.94           | 128.0             |
| 7.       | Total Utilities                     | -           | -             | 5.58           | 367.5             |
| 8.       | Other Direct (Catalyst)             | -           | -             | -              | -                 |
| 9.       | <u>TOTAL DIRECT</u>                 | -           | -             | <u>\$15.61</u> | <u>\$ 1,029.6</u> |
| 10.      | Payroll Burden                      | 30% L2      | -             | .14            | 9.3               |
| 11.      | Plant Overhead                      | 70%(L2+L3)  | -             | .38            | 25.2              |
| 12.      | Pack & Ship                         | -           | -             | -              | -                 |
| 13.      | Waste Disposal                      | 1000 MH     | 3.90          | .06            | 3.9               |
| 14.      | Other Indirect                      | -           | -             | -              | -                 |
| 15.      | <u>TOTAL INDIRECT</u>               | -           | -             | <u>\$ .58</u>  | <u>\$ 38.4</u>    |
| 16.      | Depreciation                        | 10% FC      | -             | 9.10           | 600.0             |
| 17.      | Taxes                               | 2% FC       | -             | 1.82           | 120.0             |
| 18.      | Insurance                           | 1% FC       | -             | .91            | 60.0              |
| 19.      | Other Fixed                         | -           | -             | -              | -                 |
| 20.      | <u>TOTAL FIXED</u>                  | -           | -             | <u>\$11.83</u> | <u>\$ 780.0</u>   |
| 21.      | <u>TOTAL OPERATING</u>              | -           | -             | <u>\$28.02</u> | <u>\$ 1,848.0</u> |
| 22.      | Credits                             | -           | -             | -              | -                 |
| 23.      | <u>NET OPERATING</u>                | -           | -             | <u>\$28.02</u> | <u>\$ 1,848.</u>  |

OPERATING COSTS

PROCESS: DMA Sorption

CASE NO. 2D

Fixed Capital, Battery Limits Basis  
Sulfur Production NTD x 330 Days =\$3,900,000  
66,000NTY

| Line No. | Cost Items                            | Used Per NT | Cost Per Unit | Per NT Sulfur | Per Year \$M |
|----------|---------------------------------------|-------------|---------------|---------------|--------------|
|          | DMA                                   | 1.25 lbs    | \$ .20        | \$ .25        | \$ 16.5      |
|          | Soda Ash                              | 0.02 NT     | \$40.         | .80           | 52.8         |
|          | H <sub>2</sub> SO <sub>4</sub> , 100% | 0.023 NT    | \$30.         | .69           | 45.5         |
| 1.       | Total Raw Materials                   | -           | -             | \$ 1.74       | \$ 114.8     |
| 2.       | Direct Labor                          | 8750 MH     | \$3.50        | .47           | 31.0         |
| 3.       | Supervision                           | -           | \$10,000      | .08           | 5.0          |
| 4.       | Maintenance                           | 5% FC       | -             | 2.95          | 195.0        |
| 5.       | Plant Supplies                        | 10%(L2+L3)  | -             | .05           | 3.6          |
| 6. a)    | Electricity                           | 67 KWH      | \$ .01        | .67           | 44.2         |
| b)       | Cooling Water                         | 22.0 MG     | .05           | 1.10          | 72.5         |
| c)       | Boiler Feed Water                     | - MG        | .25           | -             | -            |
| d)       | Fuel Gas                              | MCF         | .30           | -             | -            |
| e)       | Steam                                 | 3.4 M lb    | .50           | 1.70          | 112.0        |
| 7.       | Total Utilities                       | -           | -             | 3.47          | 228.7        |
| 8.       | Other Direct (Catalyst)               | -           | -             | -             | -            |
| 9.       | <u>TOTAL DIRECT</u>                   | -           | -             | \$ 8.76       | \$ 578.1     |
| 10.      | Payroll Burden                        | 30% L2      | -             | .14           | 9.3          |
| 11.      | Plant Overhead                        | 70%(L2+L3)  | -             | .38           | 25.2         |
| 12.      | Pack & Ship                           | -           | -             | -             | -            |
| 13.      | Waste Disposal                        | 1000 MH     | 3.90          | .06           | 3.9          |
| 14.      | Other Indirect                        | -           | -             | -             | -            |
| 15.      | <u>TOTAL INDIRECT</u>                 | -           | -             | \$ .58        | \$ 38.4      |
| 16.      | Depreciation                          | 10% FC      | -             | 5.91          | 390.0        |
| 17.      | Taxes                                 | 2% FC       | -             | 1.18          | 78.0         |
| 18.      | Insurance                             | 1% FC       | -             | .59           | 39.0         |
| 19.      | Other Fixed                           | -           | -             | -             | -            |
| 20.      | <u>TOTAL FIXED</u>                    | -           | -             | \$ 7.68       | \$ 507.0     |
| 21.      | <u>TOTAL OPERATING</u>                | -           | -             | \$ 17.02      | \$ 1,123.5   |
| 22.      | Credits                               | -           | -             | -             | -            |
| 23.      | <u>NET OPERATING</u>                  | -           | -             | \$ 17.02      | \$ 1,124.    |

EXHIBIT 5-9

Capacity - Cost Relation

| Case 2B (4.5% SO <sub>2</sub> ) | Per NT Sulfur  |                |                |
|---------------------------------|----------------|----------------|----------------|
|                                 | <u>200 NTD</u> | <u>100 NTD</u> | <u>400 NTD</u> |
| Fixed Capital, MM \$            | (5.0)          | (3.3)          | (7.6)          |
| Fixed Charges at 18% F.C.       | \$ 13.65       | \$ 18.00       | \$ 10.39       |
| R/M                             | 3.08           | 3.08           | 3.08           |
| Utilities                       | 4.66           | 4.66           | 4.66           |
| Direct Labor, Supv., Supplies   | .60            | 1.20           | .30            |
| Indirect Costs                  | <u>.58</u>     | <u>1.16</u>    | <u>.29</u>     |
| Total                           | \$ 22.57       | \$ 28.10       | \$ 18.72       |

| Case 2C (2.9% SO <sub>2</sub> ) | <u>200 NTD</u> | <u>100 NTD</u> | <u>400 NTD</u> |
|---------------------------------|----------------|----------------|----------------|
| Fixed Capital, MM \$            | (6.0)          | (4.0)          | (9.0)          |
| Fixed Charges at 18% F.C.       | \$ 16.38       | \$ 21.80       | \$12.30        |
| R/M                             | 4.88           | 4.88           | 4.88           |
| Utilities                       | 5.58           | 5.58           | 5.58           |
| Direct Labor, Supv., Supplies   | .60            | 1.20           | .30            |
| Indirect Costs                  | <u>.58</u>     | <u>1.16</u>    | <u>.29</u>     |
| Total                           | \$ 28.02       | \$ 34.62       | \$ 23.35       |

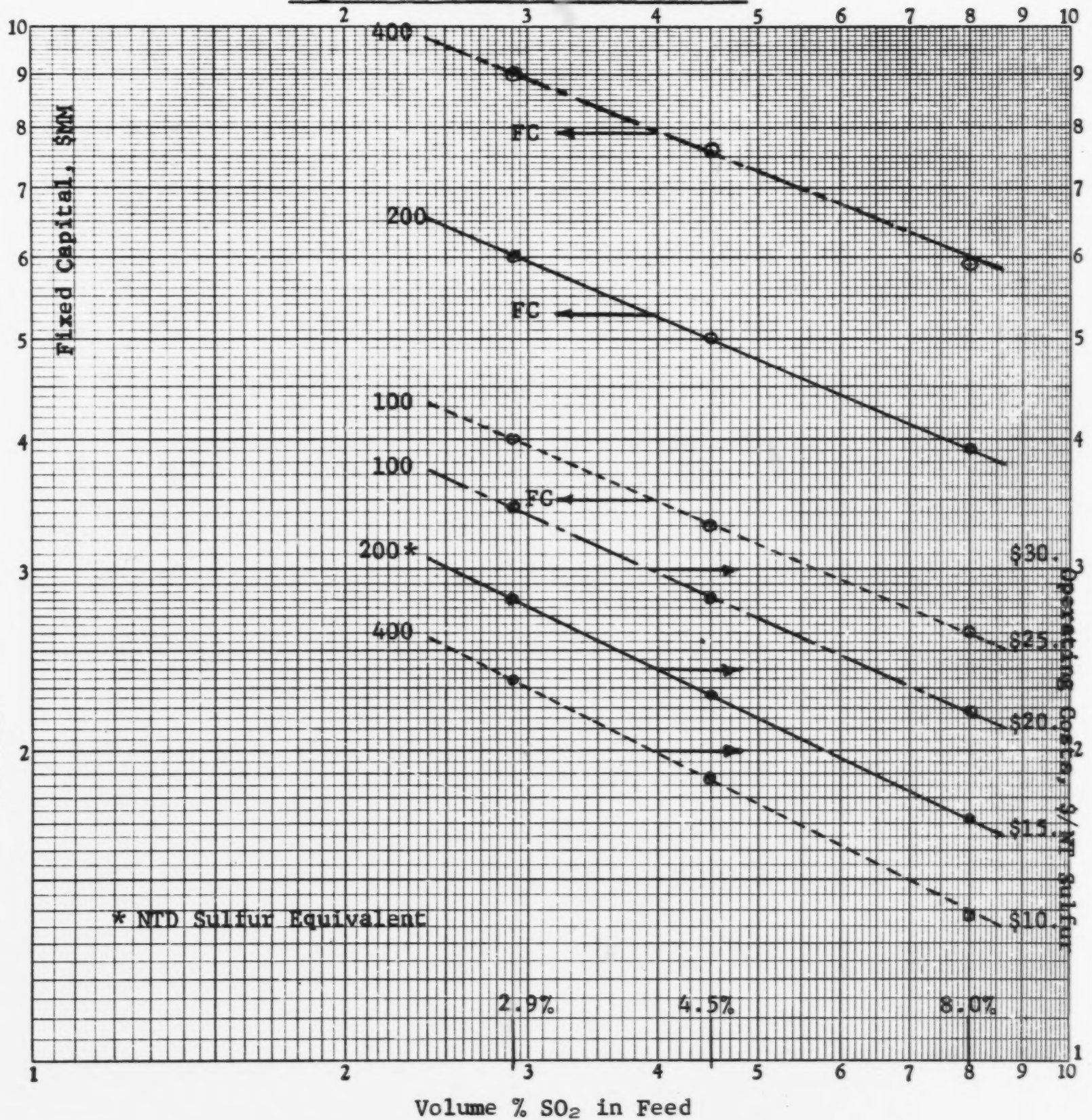
  

| Case 2D (8.0% SO <sub>2</sub> ) | <u>200 NTD</u> | <u>100 NTD</u> | <u>400 NTD</u> |
|---------------------------------|----------------|----------------|----------------|
| Fixed Capital, MM \$            | (3.9)          | (2.6)          | (5.9)          |
| Fixed Charges at 18% F.C.       | \$ 10.63       | \$ 14.20       | \$ 8.05        |
| R/M                             | 1.74           | 1.74           | 1.74           |
| Utilities                       | 3.47           | 3.47           | 3.47           |
| Direct Labor, Supv., Supplies   | .60            | 1.20           | .30            |
| Indirect Costs                  | <u>.58</u>     | <u>1.16</u>    | <u>.29</u>     |
| Total                           | \$ 17.02       | \$ 21.77       | \$ 13.85       |



# EXHIBIT 5-10

## ECONOMICS SO<sub>2</sub> CONCENTRATION BY DMA SORPTION



# EXHIBIT 5-11

## ECONOMICS SO<sub>2</sub> CONCENTRATION BY DMA SORPTION

